Learning and Labor.
LIBRARY
OF THE
University of Illinois.
CLASS. BOOK. VOLUME.
540.5 AC 25
Accession No.

532
177

AMERICAN

CHEMICAL JOURNAL

EDITED BY

IRA REMSEN

PROFESSOR OF CHEMISTRY IN THE JOHNS HOPKINS UNIVERSITY

VOL. XXV. JANUARY–JUNE. 1901.

BALTIMORE : THE EDITOR.

THE CHEMICAL PUBLISHING CO., PRINTERS,
EASTON, PA.

Contents of Vol. XXV.

No. 1.

A FURTHER INVESTIGATION OF THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID. By W. E. Henderson 1
THE COMPOSITION OF A WOOD OIL. By G. S. Fraps - - - 26
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY:
  XXVII.—*On Triphenylchlormethane.* By James F. Norris and Warren W. Sanders - - - - - - - 54
THE CONDUCTIVITIES OF SOME DOUBLE SALTS AS COMPARED WITH THE CONDUCTIVITIES OF MIXTURES OF THEIR CONSTITUENTS. By Charles F. Lindsay - - - - - - - - 62
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF LEHIGH UNIVERSITY:
  V.—*The Action of Sulphuric Acid on Phenetol.* By William B. Shober and Henry L. Bowers - - - - - - 69

NOTES.

The New Radio-active Substances - - - - - - - 77
On the Nature of the Oxyazo Compounds - - - - - 80

REVIEWS.

Chemical Technology - - - - - - - - - - 80
L'Eau dans l'Industrie - - - - - - - - - 81
The Oil Chemist's Handbook - - - - - - - - 82
Grundlinien der anorganischen Chemie - - - - - - 83
Acetylene, a Handbook for the Student and Manufacturer - - 85
Commercial Organic Analysis, Vol. III, Part I - - - - - 88

No. 2.

ON THE BEHAVIOR OF IODINE AND BROMINE TOWARDS CHLORINE HEPTOXIDE AND PERCHLORIC ACID. By Arthur Michael and Wallace T. Conn - - - - - - - - - - 89
ORTHOPHENYLSULPHONEBENZOIC ACID AND RELATED COMPOUNDS. By Hall Canter - - - - - - - - - - 96
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY:
  XXVIII.—*On the Importance of Formic Aldehyde as a Product of the Partial Combustion of Organic Compounds.* By S. P. Mulliken with J. W. Brown and P. R. French 111
  XXIX.—*On the Non-Existence of Trivalent Carbon.* By James F. Norris - - - - - - - - 117

185332

THE CONSTITUTION OF BENZENE. By George M. Richardson - 123
CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY:
XXXIX.—*The Synthesis of Amines by the Use of Alkyl Salicylates.* By Alfred Tingle - - - - - - 144

NOTES.

Argon and Its Companions - - - - - - - - - 156
The Liquefaction of Hydrogen - - - - - - - - - 160
Centenary Commemoration Lecture at the Royal Institute of Great Britain - - - - - - - - - - - 161
Fluosilicic Acid as a Preservative of Manure - - - - - 166
Ammonium Bromide and the Atomic Weight of Nitrogen - - 167
Asymmetric Optically Active Sulphur Compounds - - - 167

REVIEWS.

Die aetherischen Oele - - - - - - - - - - 168
The Volatile Oils - - - - - - - - - - - 168
A Handbook of Industrial Organic Chemistry - - - - 169
Die Glykoside - - - - - - - - - - - - 170
An Outline of the Theory of Thermodynamics - - - - 171
Corrections - - - - - - - - - - - - - 172

NO. 3.

ON THE ACTION OF AROMATIC SULPHONCHLORIDES ON UREA. By Ira Remsen and W. W. Garner - - - - - - - - 173
ON THE ACTION OF AROMATIC SULPHONCHLORIDES ON THIOUREA. By Ira Remsen and H. J. Turner - - - - - - - 190
ON THE ACTION OF THE CHLORIDES OF ORTHOSULPHOBENZOIC AND OF PARANITROORTHOSULPHOBENZOIC ACIDS ON UREA. By Willis B. Holmes - - - - - - - - - - - 202
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY:
XXX.—*On the Nature of Lead Amalgams.* By Henry Fay and Edward North, 2nd - - - - - - 216

REPORT.

The Dissociating Power of Different Solvents. A Summary - - 232

REVIEWS.

A Manual of Assaying - - - - - - - - - - 249
A Text-book of Important Minerals and Rocks - - - - 249
Elements of Mineralogy, Crystallography, and Blowpipe Analysis from a Practical Standpoint - - - - - - - 250
Lehrbuch der anorganischen Chemie - - - - - - 250
Quantitative Chemical Analysis - - - - - - - 251

No. 4.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE:
XXXV.—*On the Composition of California Petroleum.* By Charles F. Mabery and Edward J. Hudson - - 253
XXXVI.—*On the Chlorine Derivatives of the Hydrocarbons in California Petroleum.* By Charles F. Mabery and Otto J. Sieplein - - - - - - - - 284
XXXVII.—*On the Composition of Japanese Petroleum.* By Charles F. Mabery and Shinichi Takano - - - 297
THE BASIC NITRATES OF BISMUTH. By F. B. Allan - - - 307
A NEW TEST FOR CHLORINE FOR USE WITH THE BLOWPIPE. By Henry W. Nichols - - - - - - - - - 315
ON TRIVALENT CARBON. By M. Gomberg - - - - - 317

REPORTS.

International Atomic Weights - - - - - - - - 335
The Higher Superoxides of Hydrogen - - - - - - 336
A Recent View of Atomic Structure - - - - - - - 340
Combustible Gases in the Atmosphere - - - - - - 344

REVIEWS.

Air, Water, and Food from a Sanitary Standpoint - - - - 347
Evolution of the Thermometer - - - - - - - - 348

No. 5.

CONTRIBUTION TO THE STUDY OF AQUEOUS SOLUTIONS OF DOUBLE SALTS:
IV.—*Iodides, Cyanides, Nitrates, and Sulphates.* By Harry C. Jones and B. Palmer Caldwell - - - - - 349
CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF MICHIGAN:
On the Constitution of Jamaica Dogwood. By Paul C. Freer and A. M. Clover - - - - - - - - 390
THE CRYSTALLIZATION OF COPPER SULPHATE. By Arthur John Hopkins - - - - - - - - - - - - 413
ON METHYL CYANIDE AS A CATALYTIC REAGENT; AND A CRITICISM OF J. U. NEF'S VIEWS ON THE FRANKLAND, WURTZ, AND CONRAD REACTIONS. By Arthur Michael - - - - - 419
ON THE FORMATION OF PLATINUM TETRACHLORIDE FROM AQUEOUS HYDROCHLORIC ACID BY ATMOSPHERIC OXIDATION IN CONTACT WITH PLATINUM BLACK. By J. W. Mallet - - - - 430

NOTES.

Ammonium Amalgam - 431
The Density and Molecular Weight of Ozones - 432
The Lavoisier Statue in Paris - 435

REVIEWS.

Angewählte Methoden der analytischen Chemie - 437
The Chemical Analysis of Iron - 437

No. 6.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE:

On Dehydromucic Acid. By Henry B. Hill - 439
CXXI.—*On Dehydromucic Acid and Certain of Its Derivatives.* By Isaac K. Phelps and William J. Hale - 445
CXXII.—*On the Reduction of Dehydromucic Acid.* By Henry B. Hill and Alvin S. Wheeler - 463
THE CONSTITUTION OF THE OXYAZO COMPOUNDS. By Wm. McPherson and Herbert C. Gore - 485
ACTION OF PHENOLS ON ETHYLIC OXALATE. By J. Bishop Tingle and Leo O'Byrne - 496
THE DETERMINATION OF PENTOSANS. By G. S. Fraps - 501
AN EASILY CONSTRUCTED BAROMETER. By George W. Russell - 508

OBITUARY.

François Marie Raoult - 510

REPORTS.

The Action of Water upon Rocks - 511

REVIEWS.

Engineering Chemistry - 517
Anorganische Fermente - 517

Correspondence - 518
Corrections - 518
Index - 519

VOL. XXV. JANUARY, 1901. NO. 1.

AMERICAN

CHEMICAL JOURNAL

A FURTHER INVESTIGATION OF THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.[1]

BY W. E. HENDERSON.

The chloride was prepared according to the directions given by Remsen and Gray,[2] with some modifications. The dehydrated acid potassium salt of paranitroorthosulphobenzoic acid and phosphorus pentachloride, in the ratio of 40 : 55 grams, are brought together in a mortar and intimately mixed. The mixture is put into an evaporating dish and placed on a sulphuric acid bath, previously heated to 150°. As soon as the action has been well started, the dish is removed and the reaction allowed to proceed without further heating. When it is complete, and the contents of the dish has cooled down to the ordinary temperature, the oily product is poured slowly into a salt-bottle containing ice-water, the bottle being frequently shaken during the process. The chloride is then shaken with repeated portions of water, until the water remains clear after shaking, and the chloride has become semi-solid. The water is then poured off, the brownish gummy chloride dissolved in chloroform, and the solution placed in a good-sized separating funnel. Ice-water is then added, and the contents of the funnel treated with successive portions of ammonia (desk ammonia diluted one-half). Shaking is continued after each addition until the odor of ammonia has disappeared, and ice is added from time to time as may be required.

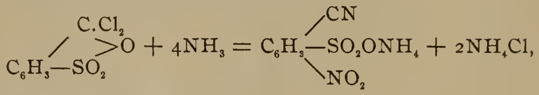
---

[1] From the author's dissertation, submitted to the Board of University Studies of the Johns Hopkins University, June, 1897, for the degree of Doctor of Philosophy. The work was undertaken at the suggestion of Professor Remsen, and carried on under his guidance.

[2] This JOURNAL, 19, 496.

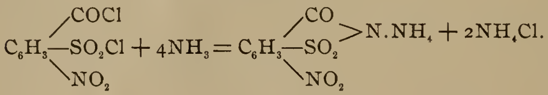
When it is found that the odor of ammonia persists after a few minutes' shaking, the chloroform layer, which is often filled with a solid substance that has separated during the process, is drawn off, filtered, and dried with calcium chloride.

By this process all of the unsymmetrical chloride is converted into the ammonium salt of paranitroorthocyanbenzenesulphonic acid, according to the equation :



$$\mathrm{C_6H_3}\begin{array}{l}\diagup \mathrm{C.Cl_2} \\ -\mathrm{SO_2}\end{array}\!\!>\mathrm{O} + 4\mathrm{NH_3} = \mathrm{C_6H_3}\begin{array}{l}\diagup \mathrm{CN} \\ -\mathrm{SO_2ONH_4} \\ \diagdown \mathrm{NO_2}\end{array} + 2\mathrm{NH_4Cl},$$

while the symmetrical chloride remains for the most part unchanged, though some of it is converted into the ammonium salt of paranitrobenzoic sulphinide :



$$\mathrm{C_6H_3}\begin{array}{l}\diagup \mathrm{COCl} \\ -\mathrm{SO_2Cl} \\ \diagdown \mathrm{NO_2}\end{array} + 4\mathrm{NH_3} = \mathrm{C_6H_3}\begin{array}{l}\diagup \mathrm{CO} \\ -\mathrm{SO_2} \\ \diagdown \mathrm{NO_2}\end{array}\!\!>\mathrm{N.NH_4} + 2\mathrm{NH_4Cl}.$$

It was found that working in this way the symmetrical chloride could be prepared in pure condition free from its isomer. The chloroform completely evaporates in a short time, leaving fine crystals of the symmetrical chloride. In case the evaporation is slow and incomplete, it may be concluded that not all of the unsymmetrical chloride has been removed. The yield was uniformly about 40 per cent of the theoretical.

From the water used to wash the chlorides a considerable amount of the original salt may be regained, as the reaction, under the conditions employed, is never complete.

An examination was made of the substance mentioned as separating in the chloroform solution of the chlorides during the treatment with ammonia, and it was found to possess the following properties: It is insoluble in benzene, chloroform, acetone, ether, and ligroin; soluble in glacial acetic acid, from which it separates, on cooling, in colorless crystalline condition; insoluble in the cold in water, alcohol, and ammonia, but by long standing in these solvents it is dissolved with decomposition. It is soluble in them on boiling, with decomposition. It was dissolved in hot water, and the solution, which was acid in reaction, was neutralized with potassium carbonate. On adding an excess of hydrochloric acid to this solution and allowing it to cool, characteristic needles of the acid potassium salt of paranitroorthosulphobenzoic acid separated. These properties identify the substance as the anhydride of this acid. The formation of the corresponding anhydride of orthosulphobenzoic acid by the action of phosphorus pentachloride upon its acid potassium salt was observed by Sohon,[1] who made use of the reaction to prepare this anhydride in quantity.

As first obtained, the crystals of the symmetrical chloride resemble irregularly-shaped pieces of amber, both in color and in luster. On recrystallization from chloroform or ether they can be obtained perfectly colorless, and are often of very simple crystallographic form. The chloride crystallizes in the monoclinic system, and possesses a very remarkable crystallizing power, in which respect it differs noticeably from its isomer. Even in chloroform solution that is far from dry, crystals appear with the greatest ease.

The habit of the crystals differs very much according to the conditions of crystallization. Not infrequently, almost perfectly formed crystals of the simplest form—the oblique octahedron—were obtained, though for the most part the forms were much more complicated, pinacoid and dome faces, together with basal planes, being prominent. As a rule, the crystals were not suitable for crystallographic work, as the faces are rough, owing to the great solubility of the chloride. By proper precautions, however, fairly good ones were obtained for this purpose. The size of some of the crystals obtained was unusual for substances of this class. One crystal obtained with no special precautions, save letting a solution of the chloride stand undisturbed for several days, in a rather cool place, measured 3 × 2.5 × 1.5 cm., and weighed 11.2 grams.

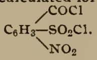
---

[1] This JOURNAL, **20**, 257.

The crystals are quite compact, their density being about 1.85. They melt at 98° (uncorr.). The chloride is quite stable when crystallized. Even in moist air the crystals were unchanged and retained their luster as long as they were in my possession.

An analysis for chlorine gave the following results:

0.2200 gram substance gave 0.2212 gram AgCl.

	Calculated for  $C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl.\\ \diagdown NO_2\end{array}$	Found.
Cl	24.94	24.83

A crystallographic examination of the usual form of the crystals was made by Dr. F. P. King, in the mineralogical laboratory, and his measurements and description are here given:

System monoclinic.

$s = +\frac{1}{2}P\overline{\infty} = (201)$

$o = +P = (111)$

$c = +P\overline{\infty} = (011)$

$m = \infty P = (110)$

$s : m' = 97° 35'$

$s : o = 120° 26'$

$s : c = 132° 45'$

$o : o = 96° 20'$

$o : c = 138° 10'$

$o : m' = 87° 31'$

$o : m = 138° 01'$

$m : m = 116° 50'$

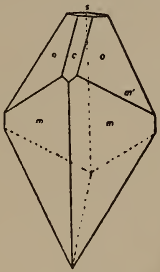
$m : m' = 63° 10'$

$m : c = 122° 19'$

$\grave{a} : b : \dot{c} :: 0.898321 : 1 : 1.114179$

$\beta = 43° 11' 17''$

The figure is drawn on Dana's axes, showing β in front. Distortion, due to irregular growth, causes planes ċ and s generally to disappear at one extremity of ć axis.



Since merohedrism is invariably present in respect to these planes the figure is drawn conformable to this distortion.

The measurements given are the actual measurements.

Action of Aluminium Chloride and Benzene upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

Hollis,[1] in his study of the action of these reagents upon the unsymmetrical chloride, tested their action upon one portion of the symmetrical chloride, and found the products to be identical in the two cases. A few experiments were made in confirmation of these results, and the same products, in general, were obtained. It was observed, however, that the reactions differ in the relative ease with which they are brought about. In the case of the symmetrical chloride, the reaction is a more vigorous one. On adding aluminium chloride to a solution of the symmetrical chloride in benzene, action begins at once at the temperature of the hand, and very little external heat, and that only in the latter stages of the operation, is required to complete the reaction. The application of much heat converts all of the product into thick tarry substances, from which nothing satisfactory could be obtained.

When the reaction was complete, the resulting product was isolated and purified in accordance with the directions given by Hollis. Repeated trials showed that, as in the case of the unsymmetrical chloride, only one phenyl group could be introduced by this method. The resulting compound, paranitroorthobenzoylbenzenesulphone chloride, was identical with that derived from the unsymmetrical chloride. Owing, however, to the fact that so much more decomposition occurs in the reaction with the symmetrical chloride, the paranitroorthobenzoylbenzenesulphone chloride could not be obtained in perfectly pure condition. In appearance it agreed closely with that described by Hollis, forming very characteristic, greenish, rhombic crystals. These melted, not very sharply, at 174° instead of 177°, as observed by Hollis. Accordingly, to establish the identity of the two compounds, beyond any doubt, the material on hand was converted into the barium salt of paranitroorthobenzoylbenzenesulphonic acid. This was done by boiling the sulphone chloride with dilute hydrochloric acid until complete solution was effected; evaporating to dryness on a water-bath; dissolving the residue in hot water; and neutralizing with barium carbonate. On filtering the hot solution, and allowing it to cool, the barium salt separated.

---

[1] This JOURNAL, **23**, 233.

The solution was slightly colored by impurities, and the long needles in which the salt crystallized were also somewhat colored. They were analyzed with the expectation that they would prove to be specimens of the salt described by Hollis as having 3 or 3.5 molecules of water of crystallization, inasmuch as they were formed under conditions favorable to the formation of salts of this particular type. Hollis found that this salt could be obtained with at least four different ratios of water of crystallization; *viz.*, 3, 3.5, 6, and 7 molecules, respectively.

The analysis gave the following results:

0.3087 gram substance lost 0.064 gram H_2O at 210°, and gave 0.0759 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 11H_2O$.	Found.
H_2O	20.90	20.73
Ba	18.29	18.23

The mother-liquor, in which the crystals remaining from analysis were redissolved, was warmed, but not boiled, with bone-black to remove impurities. When filtered the solution was perfectly colorless, and on standing for some time, well formed, colorless, rhombic crystals appeared.

On analysis they gave the following results :

0.2804 gram substance lost 0.0405 gram at 210°, and gave 0.0736 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$.	Found.
H_2O	14.40	14.44
Ba	18.29	18.03

On making a further supply of the salt, it was found that if the solution, after filtering from the excess of barium carbonate, was diluted to such an extent that no crystals separated on cooling, then, on slow evaporation under a bell-jar, the first crystals to appear were very long needles. As evaporation proceeded, these needles became much thicker, assuming prismatic proportions, and corresponded in appearance to the salt described by Hollis as having 6 molecules of water of crystallization. As growth proceeded, the crystals became dark in color, and the mother-liquor correspondingly clearer. Evidently the crystals absorbed the colored impurities in their growth. When the solution had become quite colorless, rhombic crystals of the salt containing 7 molecules of water of crystallization appeared. The larger prismatic crystals were carefully removed, and redissolved in water in order to see if the same phenomena would repeat themselves. This was in fact found to be the case, crystals of both types resulting. Without separating the crystals in this second experiment, water was added, and the crystals dissolved. The solution was then warmed briskly with bone-black, and filtered. From the filtrate, which was now colorless, nothing but the rhombic crystals having 7 molecules of water of crystallization could be obtained, although the conditions were widely varied.

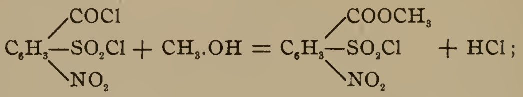
Analysis of these last crystals gave the following results :

0.2400 gram substance lost 0.035 gram at 210°, and gave 0.0637 gram $BaSO_4$.

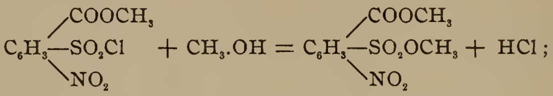
	Calculated for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$.	Found.
H_2O	14.40	14.58
Ba	18.29	18.27

Action of Alcohols upon the Symmetrical Chloride of Paranitro-orthosulphobenzoic Acid.

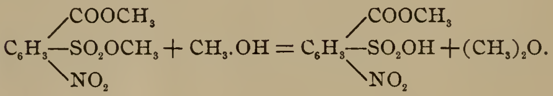
Kastle[1] found that when the chloride of paranitroorthosulphobenzoic acid (which he supposed to be an individual) was dissolved in alcohol and the solution boiled for some time, the acid ethereal salt of paranitroorthosulphobenzoic acid was the final product:

(1) 

$$C_6H_3\left\{\begin{array}{l}COCl\\SO_2Cl\\NO_2\end{array}\right. + CH_3.OH = C_6H_3\left\{\begin{array}{l}COOCH_3\\SO_2Cl\\NO_2\end{array}\right. + HCl;$$

(2) 

$$C_6H_3\left\{\begin{array}{l}COOCH_3\\SO_2Cl\\NO_2\end{array}\right. + CH_3.OH = C_6H_3\left\{\begin{array}{l}COOCH_3\\SO_2OCH_3\\NO_2\end{array}\right. + HCl;$$

(3) 

$$C_6H_3\left\{\begin{array}{l}COOCH_3\\SO_2OCH_3\\NO_2\end{array}\right. + CH_3.OH = C_6H_3\left\{\begin{array}{l}COOCH_3\\SO_2OH\\NO_2\end{array}\right. + (CH_3)_2O.$$

Kastle, it will be observed, gave the symmetrical formula to this mixture of chlorides. Several acid-ethereal salts were made, and a series of neutral salts of various metals described by him.

The action of the pure symmetrical chloride was studied in the same general manner, to see if the resulting products are the same as those resulting from the mixed chlorides.

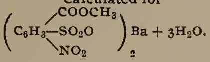
1. *Action of Methyl Alcohol.*—A portion of the chloride was dissolved in methyl alcohol and the solution boiled until a drop added to water gave no precipitate of unchanged chloride. The alcohol was then distilled off, and the thick syrup remaining diluted with water. This was neutralized with barium carbonate and filtered. On cooling, the barium salt crystallized in shining mica-like plates, or in yellowish needles agreeing closely with the description given by Kastle.

Analysis:

0.2664 gram substance lost 0.0211 gram H_2O at 150°, and gave 0.0870 gram $BaSO_4$.

---

[1] This JOURNAL, II, 181.

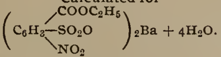
	Calculated for  $\left(C_6H_3\begin{smallmatrix}COOCH_3\\ -SO_2O\\ NO_2\end{smallmatrix}\right)_2Ba + 3H_2O.$	Found.
H_2O	7.59	7.88
Ba	20.85	20.85

2. *Action of Ethyl Alcohol.*—In like manner the barium-ethyl salt was made. It also agreed perfectly with Kastle's description, crystallizing in fine, colorless needles forming tufts, from a not too concentrated solution. In case it is necessary to concentrate these solutions, it is of advantage to add a small quantity of alcohol to the solution, as this prevents any great amount of saponification, which otherwise takes place to a noticeable extent.

Analysis :

I. 0.2824 gram substance lost 0.0276 gram at 180°, and gave 0.0860 gram $BaSO_4$.

II. 0.2655 gram substance lost 0.0262 gram H_2O at 190°, and gave 0.0815 gram $BaSO_4$.

	Calculated for  $\left(C_6H_3\begin{smallmatrix}COOC_2H_5\\ -SO_2O\\ NO_2\end{smallmatrix}\right)_2Ba + 4H_2O.$	Found.	
		I.	II.
H_2O	9.51	9.77	9.86
Ba	20.00	19.84	20.02

Kastle also found that by dissolving the mixed chlorides in cold alcohol, and allowing the solution to evaporate spontaneously, there separated crystals of the chloride of the acid ethereal salt of paranitroorthosulphobenzoic acid represented in equation (1). This same product was sought for, when pure symmetrical chloride was employed, but without success. Under all conditions crystals of unchanged chloride separated, or else it was found that it had been converted into the acid ethereal salt. In another trial, cold water was carefully added in small portions, since Kastle found that such treatment facilitated the separation of the substance ; the chloride alone appeared. Still other attempts were made to obtain the substance by adding a large amount of water to the solution of the chloride in alcohol, after it had stood for some time. In this way quite a precipitate was thrown down, and this was filtered off and crystallized from ether. It always proved to be the symmetrical chloride, and none of the other substance was obtained.

Remsen and Karslake,[1] in working with the symmetrical chloride of orthosulphobenzoic acid, were unable to isolate the analogous compound, although from the mixed chlorides, by the action of alcohols, Remsen and Dohme[2] had obtained chloroethereal salts.

Inasmuch as the pure symmetrical chloride is relatively stable in cold alcohol, it can even be crystallized from warm alcohol with very little loss. It is possible that it is more stable than the chloroethereal salt, and that in consequence the latter, when formed, yields more readily to the further action of the alcohol than the chloride does. Hence, when the action begins it at once proceeds to the limit. The fact that the symmetrical chloride is rather sparingly soluble in cold alcohol, making the use of a concentrated solution impossible, may also be a factor in the case. Whatever may be the cause, the substance could not be obtained under any conditions that were devised.

Having in my possession a very small specimen of crystallized unsymmetrical chloride, it was submitted to the action of ethyl alcohol, under as nearly as possible the conditions employed by Kastle.

Crystals of a colorless substance were obtained, which in every respect agreed with Kastle's description of the chloride of the acid ethyl ethereal salt of paranitroorthosulphobenzoic acid. Crystallized from ether, they melted at 68°.

The conditions employed by Kastle in preparing the chloride would undoubtedly lead to a relatively large proportion of the unsymmetrical chloride, and it is to this chloride that the formation of the chloroethereal salt is apparently due.

The Action of Phenols upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

Remsen and Saunders,[3] in their investigation of the chlorides of orthosulphobenzoic acid, studied the action of phenol upon these substances, and from both the symmetrical chloride and the mixed chloride they obtained a normal diphenyl ether, and a red substance which was not further studied. It was formed in small quantity, and was probably the corresponding sulphonphthaleïn. Later Remsen and McKee[2] obtained these same substances from both the symmetrical and unsymmetrical chlorides of the same acid. R. Meyer[3] obtained analogous substances by the action of various phenols upon phthalyl chloride. It seemed probable, therefore, that the chlorides of paranitroorthosulphobenzoic acid would yield similar derivatives, and a study was made of the reaction of the symmetrical chloride with a series of phenols. The products in some instances were exceedingly difficult to deal with, possessing properties that made it impossible to prepare them for analysis, but even in such cases there could be little doubt as to the general nature of the reactions that took place.

---

[1] This JOURNAL, **18**, 819.

[2] *Ibid.*, **11**, 341.

[3] *Ibid.*, **17**, 347.

1. *Action of Phenol.*—A portion of the symmetrical chloride was brought together with somewhat more than double the molecular weight of phenol. The mixture was placed in a good-sized test-tube, and the temperature gradually raised by means of a sulphuric-acid bath. As soon as the phenol melts some slight action occurs, as is indicated by the bright-red color which the liquid assumes. At 115° hydrochloric acid is freely evolved, and the action is complete at 125°. The temperatures were ascertained by the use of a thermometer as a stirring rod. During the heating the color becomes a much more intense red, growing darker in shade, while the mixture becomes somewhat viscous, but does not solidify while hot.

When cool, the solid product was repeatedly extracted with boiling water, the aqueous solution being deep-purple. The colored material was very slowly removed from the insoluble residue in this manner, and so the process was continued with dilute alkali. The solid residue was dissolved in alcohol, purified with bone-black, and filtered. On cooling, needles of a straw-yellow color separated, which melted at 119° (uncorr.).

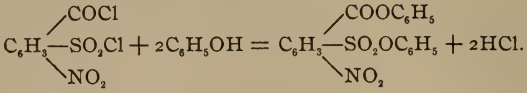
These proved to be the normal diphenyl ester of paranitro-

---

[1] This JOURNAL, **18**, 798.

[2] Ber. d. chem. Ges., **26**, 204.

orthosulphobenzoic acid, the formation of this substance being expressed by the equation :



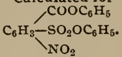
$$C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + 2C_6H_5OH = C_6H_3\begin{array}{l}\diagup COOC_6H_5\\ -SO_2OC_6H_5\\ \diagdown NO_2\end{array} + 2HCl.$$

Analyses gave the following results :

I. 0.1627 gram substance gave 0.3398 gram CO_2 and 0.0510 gram H_2O.

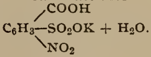
II. 0.1999 gram substance gave 0.4180 gram CO_2 and 0.0600 gram H_2O.

III. 0.2649 gram substance gave 0.1561 gram $BaSO_4$.

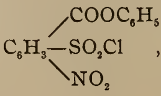
	Calculated for  $C_6H_3\begin{array}{l}\diagup COOC_6H_5\\ -SO_2OC_6H_5.\\ \diagdown NO_2\end{array}$	Found.		
		I.	II.	III.
C	57.14	56.97	57.03	....
H	3.26	3.47	3.33	....
S	8.02	....	....	8.09

The substance possesses properties similar to those of the diphenyl ester of orthosulphobenzoic acid described by Remsen and Saunders. It is insoluble in water, and is not affected by hydrochloric acid or aqueous alkali. On heating for a short time with alcoholic potash the needles were transformed into a voluminous precipitate. This was filtered off, dissolved in water, and hydrochloric acid was added. On cooling, characteristic crystals of the acid potassium salt of paranitroorthosulphobenzoic acid separated. Analysis :

0.1392 gram substance lost 0.009 gram at 150° and gave 0.0385 gram K_2SO_4.

	Calculated for  $C_6H_3\begin{array}{l}\diagup COOH\\ -SO_2OK + H_2O.\\ \diagdown NO_2\end{array}$	Found.
H_2O	5.95	6.51
K	13.65	13.35

No attempt was made to isolate the intermediate chloroethereal salt of the composition,



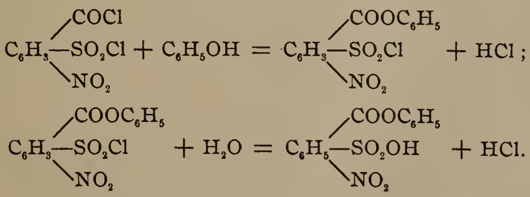
$$C_6H_3\begin{array}{l}\diagup COOC_6H_5\\ -SO_2Cl\\ \diagdown NO_2\end{array}$$

, or its amide

as was done by Remsen and McKee[1] in the case of the analogous ester of orthosulphobenzoic acid.

On evaporating the aqueous extract from the original insoluble residue almost to dryness on the water-bath, there was a deposit on the sides of the dish of scales possessing a beautiful bronze-green metallic luster. They formed a deep purple solution in alkalies, or magenta if the solution was very dilute, and orange-yellow in acids. On acidifying the alkaline extract with hydrochloric acid, this same substance was precipitated as a brownish, flocculent precipitate. It was, however, found to be impossible to obtain it in pure condition. The amount formed in the reaction is small, and its properties were such as to render work with it very difficult. The method of preparation is not satisfactory because, owing to the fact that the substance is soluble in acid solutions to an unusual extent for substances of this class, the solution had to be concentrated to such a degree as to render the precipitated substance very impure from acids and alkali salts. These could not be washed out without again dissolving the substance. From its properties, however, and its color reactions, there can be little doubt that the substance is a sulphonphthaleïn. It is always formed in considerable quantities in the reaction of phenol upon the symmetrical chloride.

It was noticed that the aqueous extract of the mass left after fusion was almost always decidedly acid in reaction, and it was thought that this might be due to the formation of an acid ethereal salt, whose formation could be thus expressed :



$$C_6H_3\begin{matrix}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{matrix} + C_6H_5OH = C_6H_3\begin{matrix}\diagup COOC_6H_5\\ -SO_2Cl\\ \diagdown NO_2\end{matrix} + HCl;$$

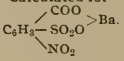
$$C_6H_3\begin{matrix}\diagup COOC_6H_5\\ -SO_2Cl\\ \diagdown NO_2\end{matrix} + H_2O = C_6H_5\begin{matrix}\diagup COOC_6H_5\\ -SO_2OH\\ \diagdown NO_2\end{matrix} + HCl.$$

Accordingly, the solution was saturated with barium carbonate. Crystals, in the form of pearly scales, separated, which upon analysis proved to be the neutral barium salt of paranitroorthosulphobenzoic acid.

---

[1] This JOURNAL, 18, 799.

0.2291 gram anhydrous salt gave 0.1386 gram $BaSO_4$.

	Calculated for  $C_6H_3\begin{array}{l} / COO \\ - SO_2O \\ \backslash NO_2 \end{array}{>}Ba.$	Found.
Ba	35.85	35.57

This seems to indicate that the reaction is an incomplete one, even in the presence of an excess of phenol. No indication of an acid ester was observed.

2. *Action of Orthocresol.*—With orthocresol the reaction proceeds with more difficulty. A higher temperature was required (135° to 145°), and quite an amount of tarry material was obtained from which very little could be extracted. The product was warmed repeatedly with dilute alkali, the solution so obtained neutralized with hydrochloric acid, and distilled with steam for several hours to free it from cresol. The resulting solution was then evaporated to a small volume, and acidified with hydrochloric acid. A considerable precipitate was thrown down, which was easily filtered off and dried. In this condition it was a dark purple-red powder, lumps of which possessed a yellowish-bronze metallic luster. In dilute alkaline solution it forms a deep bluish-purple solution, while in acids it is crimson, or light-yellow if the solution is very dilute. It is an excellent indicator, especially with ammonia.

In the insoluble tarry substance the ester was sought for and obtained in small quantity only. As all of the tarry substance is soluble in alcohol and separates again from it on cooling, in much the same condition, the ethereal salt could not be isolated by crystallization from this solvent. By boiling the substance with benzene, purifying the filtrate with bone-black, and allowing the benzene to evaporate, an almost colorless, gummy substance was obtained, which, when dissolved in alcohol, crystallizes in small, colorless needles, which melt at 89° to 90°. They were not obtained in quantity sufficient for analysis, but there was no doubt that they were crystals of the diorthocresyl ester.

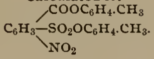
Apparently much more decomposition occurred in this reaction than when paracresol was employed, probably in consequence of the higher temperature required for the reaction.

3. *Action of Paracresol.*—This reaction was conducted in the same manner as with phenol. No hydrochloric acid was evolved until a temperature of about 110° was reached, although after melting, the solution had steadily darkened to a deep, reddish-brown color. At 130°, after heating for several hours, hydrochloric acid ceased to be evolved. The product was treated as in the last experiment. The alkaline extract did not exhibit any marked color reactions, such as were observed in most of these experiments, being dull reddish-brown in both acid and alkaline solution.

The insoluble residue crystallized from alcohol in light-brownish, transparent crystals, which did not lose their color by repeated crystallization and boiling with bone-black. They melted at 117°. From benzene they crystallized in colorless needles or flat, narrow plates. These became opaque on exposure to the air, apparently through loss of benzene of crystallization.

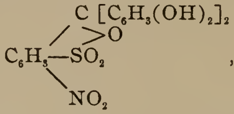
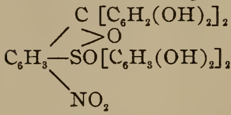
I. 0.2372 gram of the substance gave 0.5137 gram CO_2 and 0.0965 gram H_2O.

II. 0.2223 gram substance gave 0.1203 gram $BaSO_4$.

	Calculated for  $C_6H_3\begin{cases}COOC_6H_4.CH_3\\ SO_2OC_6H_4.CH_3.\\ NO_2\end{cases}$	Found.	
		I.	II.
C	59.08	59.06	....
H	3.98	4.52	....
S	7.49	....	7.43

4. *Action of Hydroquinone.*—Action with hydroquinone occurs at 120° to 135°, the mixture at the same time becoming dark colored and viscous. On cooling, the product was powdered and treated with dilute alkali. It readily dissolved, without residue, forming a dark-red solution. In concentrated solution the addition of acid produces a voluminous precipitate, dark-brown in color, which, when washed and dried on paper, forms an almost black powder. A dilute solution of this powder is dark-red when alkaline, orange-yellow when acid.

From the way in which this powder was obtained, and owing to the fact that its solubility prevented repeated washing, it was evident that it would not give close analytical results for a definite formula. It was thought, however, that analysis would give a general idea of the composition.

Analyses of different specimens gave results for sulphur, which averaged about 5.5 per cent. The percentage required for the formula  $\begin{array}{l} \quad C\,[C_6H_3(OH)_2]_2 \\ \quad / \;\; >O \\ C_6H_3-SO_2 \\ \quad \backslash \\ \quad NO_2 \end{array}$, which represents the simplest fluoresceïn, is 7.43. The compound could hardly have been so far from pure as to occasion such a discrepancy in results as this. It would appear, therefore, that more than two molecules of hydroquinone enter into reaction with one molecule of the chloride. Should four molecules be involved in the reaction, leading to a compound of some such formula as  $\begin{array}{l} \quad C\,[C_6H_2(OH)_2]_2 \\ \quad / \;\; >O \\ C_6H_3-SO[C_6H_3(OH)_2]_2 \\ \quad \backslash \\ \quad NO_2 \end{array}$, the theoretical percentage of sulphur would be 6.00, which corresponds much more closely with the results obtained.

This is in accord with the observations of a number of workers in this laboratory—Lyman, Gilpin, Linn, and others who have worked on various sulphonfluoresceïns, and have found that in many cases four, six, and even eight phenol residues condense with one molecule of the anhydrous acid. Lyman[1] especially describes a tetrahydroquinone sulphonfluoresceïn derived from orthosulphoparatoluic acid. No ester was obtained.

5. *Action of Resorcin.*—The reaction of the chloride with resorcin is a much cleaner one and proceeds more readily than in the cases just described, leading, apparently, to an individual, well-characterized compound. During the reaction, which is complete at 125°, the mixture becomes almost perfectly solid, and when cool is quite brittle. It was reduced

---

[1] This Journal, 16, 525.

to a reddish powder, and dissolved in sodium hydroxide, there being no insoluble residue. By the addition of an acid the sulphonfluoresceïn was thrown down as a chocolate-brown precipitate.

This was washed repeatedly by decantation and upon the filter, and was finally collected and dried on drying-paper. In this condition it is a light chocolate-brown powder. In dilute alkaline solution it possesses a slight fluorescence, being pink by transmitted and yellow by reflected light, suggesting eosin in a general way. It is interesting to note that the sulphonfluoresceïn of orthosulphobenzoic acid possesses a fluorescence which is almost indistinguishable from ordinary fluoresceïn, and that the introduction of a nitro group into the acid residue affects the color very much as the introduction of four bromine atoms into fluoresceïn. In acid solution the color is reddish-orange. Analyses of the compound gave the following results :

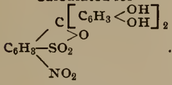
I. 0.1745 gram substance gave 0.3339 gram CO_2 and 0.059 gram H_2O.

II. 0.1467 gram substance gave 0.2820 gram CO_2 and 0.0432 gram H_2O.

III. 0.1732 gram substance gave 0.3345 gram CO_2 and 0.0571 gram H_2O.

IV. 0.2000 gram substance gave 0.1104 gram $BaSO_4$.

V. 0.1505 gram substance gave 0.0820 gram $BaSO_4$.

	Calculated for			Found.		
		I.	II.	III.	IV.	V.
C	52.66	52.18	52.42	52.67	....	....
H	3.46	3.76	3.27	3.66	....	....
S	7.39	....	....	....	7.57	7.48

An effort to obtain the anhydride was not successful. Some loss of weight was observed, but before the loss corresponded to one molecule of water the substance underwent deeper decomposition.

6. *Action of Pyrogallol.*—The product of this action dissolves readily in alkali, producing a very deep purple-black

color in concentrated solution, passing to grayish-violet as the solution is diluted. On the addition of acid it is precipitated as a black gelatinous mass. On attempting to collect the precipitate, it forms a sticky, black mass, which cannot be filtered successfully. It is best to evaporate to dryness, before filtration, and powder the residue. The powder can then be washed fairly clean. No ethereal salt was formed.

An estimation of sulphur showed that in this galleïn, as in the case of the phthaleïn derived from hydroquinone, more than two pyrogallol residues had entered the acid residue. The indications were that six molecules had entered into one of the chloride. This also agrees with the observations of Lyman,[1] who describes a hexapyrogallol galleïn of orthosulphoparatoluic acid. Probably a mixture of varying composition was obtained, and little importance was attached to the results save that they showed that no ester was formed in the reaction.

7. *Action of β-Naphthol*—It was hoped that here, as in the case of other monohydroxyphenols, an ester would be obtained. It was found, however, that very little action occurred, except such as was indicated by the development of a bright carmine color, until a temperature of 160° was reached. At this point hydrochloric acid was evolved, but the chloride itself undergoes decomposition. Nothing definite could be isolated from the reaction-products except unchanged β-naphthol.

Action of Aniline on the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

This action was studied to some extent by Remsen and Gray, but some points required further investigation. Some time was spent in an endeavor to obtain a method by which a good yield of the fusible or symmetrical anilide could be obtained. The yield in all cases tried is poor. The presence of the nitro group appears to complicate the reaction, leading to a secondary reaction, the course of which could not be followed. Upon bringing aniline and the chloride together a very vivid color was always observed, and the same was true when it was necessary to employ alkali. The fact that such colors develop when nitro compounds are treated with alkali has been noticed in many instances, and some progress has been made in the study of these compounds. Jackson and Ittner[1] have recently reviewed this subject. If a solution of the symmetrical chloride in ether is slowly added to a similar solution of aniline, no appreciable amount of heat is generated. If the resulting solution is allowed to stand at the temperature of the room, action proceeds very slowly. The extent to which the action has progressed may be followed by observing the amount of aniline hydrochloride precipitated, as the other products of the reaction are soluble in ether. In this way it was found that 5 grams of chloride required about fifty hours for its conversion into anilide and anil. Results of an entirely similar character were obtained with chloroform as the solvent. By boiling the solution for an hour or so the reaction is complete.

---

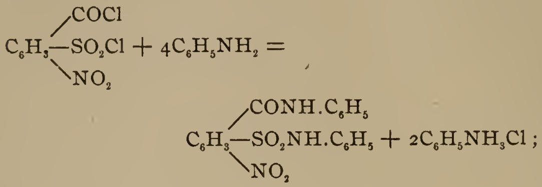
[1] This Journal, **16**, 527.

The method employed was to bring the chloride and an excess of aniline—somewhat more than four molecules—together in chloroform solution. The solution was then boiled for about an hour, after which the chloroform was distilled off. During the boiling, as well as the distillation, more or less bumping occurs in consequence of the separation of aniline hydrochloride, and constant shaking of the flask is sometimes necessary. The residue, which is in a thick, gummy condition, in consequence of the presence of an excess of aniline, was digested with water acidulated with hydrochloric acid. The excess of aniline is thus removed and the reaction-product obtained as a reddish-brown solid substance. This was treated with dilute sodium hydroxide, in the cold, all lumps of the solid substance being broken up with a stirring rod. The undissolved substance is largely the anil. This was filtered off. The anilide which is in solution is obtained by acidifying the alkaline solution. It separates immediately as a curdy, colorless precipitate, though it is frequently discolored by impurities. In such case it was generally easily purified by redissolving in alkali and pouring the solution into a slight excess of acid.

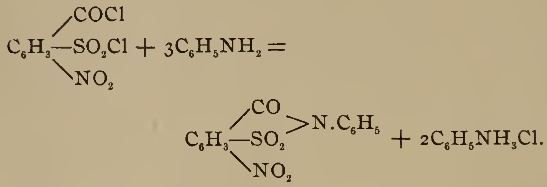
---

[1] This JOURNAL, 19, 199.

In all cases a considerable amount of anil was observed. This was true even when the ratio of chloride to aniline was as great as one molecule to eight or ten. The reactions involved are:



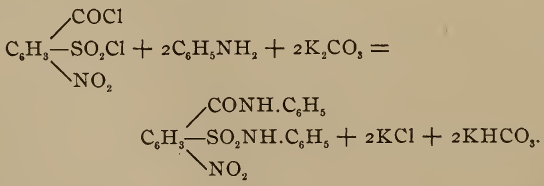
$$C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + 4C_6H_5NH_2 = C_6H_3\begin{array}{l}\diagup CONH.C_6H_5\\ -SO_2NH.C_6H_5\\ \diagdown NO_2\end{array} + 2C_6H_5NH_3Cl;$$



$$C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + 3C_6H_5NH_2 = C_6H_3\begin{array}{l}\left.\begin{array}{l}\diagup CO\\ -SO_2\end{array}\right>N.C_6H_5\\ \diagdown NO_2\end{array} + 2C_6H_5NH_3Cl.$$

On the whole, the reaction seemed to take place most satisfactorily in chloroform solution.

A number of experiments were made to see if the yield could be increased by employing a modification of the Schotten-Baumann reaction[1] for the preparation of anilides. For this purpose an ethereal solution of the chloride was added to a like solution of aniline, in which was suspended anhydrous potassium carbonate. The proportions of the substances were those demanded by the equation:



$$C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + 2C_6H_5NH_2 + 2K_2CO_3 = C_6H_3\begin{array}{l}\diagup CONH.C_6H_5\\ -SO_2NH.C_6H_5\\ \diagdown NO_2\end{array} + 2KCl + 2KHCO_3.$$

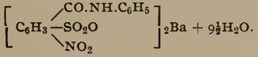
Very little anilide was, however, obtained, but in its place a substance soluble in water, of acid reaction, capable of forming salts and yielding several well characterized derivatives.

---

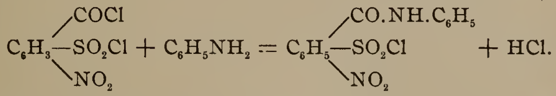
[1] Ber. d. chem. Ges., **17**, 2545; **23**, 3430.

The acid substance appeared to be an anilido acid. The barium salt was extremely soluble, crystallizing when the solution had gone nearly to dryness in thick radiating needles. Only a small amount was obtained, and it was undoubtedly impure. The analysis gave the following results :

0.2225 gram salt lost 0.0405 gram H_2O and gave 0.0530 gram $BaSO_4$.

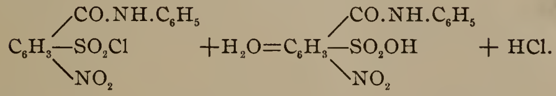
	Calculated for  $\left[C_6H_3\left\{\begin{array}{l}CO.NH.C_6H_5\\SO_2O\\NO_2\end{array}\right.\right]_2Ba + 9\frac{1}{2}H_2O.$	Found.
Ba	14.42	14.00
H_2O	18.00	18.20

There was, of course, no evidence as to which acid group combines with the aniline residue. The formation of this substance could be explained by the following reactions :

1. 

$$C_6H_3\left\{\begin{array}{l}COCl\\SO_2Cl\\NO_2\end{array}\right. + C_6H_5NH_2 = C_6H_5\left\{\begin{array}{l}CO.NH.C_6H_5\\SO_2Cl\\NO_2\end{array}\right. + HCl.$$

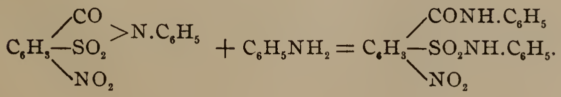
2. $K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O.$

3. 

$$C_6H_3\left\{\begin{array}{l}CO.NH.C_6H_5\\SO_2Cl\\NO_2\end{array}\right. + H_2O = C_6H_3\left\{\begin{array}{l}CO.NH.C_6H_5\\SO_2OH\\NO_2\end{array}\right. + HCl.$$

The anilide is rather sparingly soluble in alcohol, from which it is deposited, on cooling, in microscopic needles. These melt at 222°, as stated by Remsen and Gray. It is also soluble in chloroform, ether, and glacial acetic acid, but does not form well defined crystals from any solvent. It is soluble in alkali, and is reprecipitated by acids unchanged.

The anil is also soluble in alcohol, glacial acetic acid, etc. It crystallizes in much better formed needles than does the anilide. These melt at 183°. On boiling the anil for some time with aniline it is converted into the anilide :

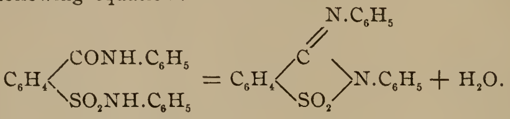


$$C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.\!\!\begin{array}{l}\\[-1em]>N.C_6H_5\\ \end{array} + C_6H_5NH_2 = C_6H_3\left\{\begin{array}{l}CONH.C_6H_5\\SO_2NH.C_6H_5.\\NO_2\end{array}\right.$$

In none of these reactions was any infusible aniline observed.

Action of Phosphorus Oxychloride on the Fusible Anilide.

Remsen and Hunter[1] found that when either of the anilides of orthosulphobenzoic acid is treated with phosphorus oxychloride, or similar dehydrating agents, a molecule of water is abstracted with the formation of a new substance. A careful study of the compound led to the belief that it is a dianil, and that its formation and structure are expressed in the following equation:



A corresponding study of the fusible anilide of paranitroorthosulphobenzoic acid was undertaken. The method employed in this study was as follows: A tubulated retort of convenient size was fused to the inner tube of a small condenser. This was done to avoid rubber connections which are attacked by phosphorus oxychloride. Another satisfactory plan is to have the neck of the retort of the same size as the inner tube of the condenser. The ends are placed in contact and the tubes bound in position by wrappings of asbestos paper. Over the joint so made a tight rubber tube is drawn.

A convenient amount (50 cc.) of phosphorus oxychloride was placed in the retort, and the anilide (5 grams) added through the tubulus. On boiling with an inverted condenser, the anilide soon dissolved with evolution of hydrochloric acid, and the solution became yellow or orange in color. The boiling was continued as long as hydrochloric acid was evolved. The oxychloride was then distilled off under diminished pressure, care being taken to shake the retort constantly during the distillation, as toward the end of the operation there is a tendency to bump violently, if this precaution is omitted. The product remaining, spattered over the walls of the retort, is a greenish-yellow solid. Water was then added, and the whole allowed to stand for a few hours to dissolve the phosphoric acid formed in the reaction. In case the anilide is not perfectly dry, a more energetic reaction occurs, and on distilling off the oxychloride, the product remains as a dark, gummy substance. This should be spread over the sides of the retort while still warm. On cooling, water is added, and gradually the gum disappears, and in its place is found the same yellow product just described. After drying this substance, it can be crystallized from acetone, benzene, or glacial acetic acid, after purification with bone-black. From these solvents it crystallizes in small yellow needles resembling quinone. From acetone the needles are more orange in color than those from glacial acetic acid, apparently because of their greater compactness. In case glacial acetic acid is used, care should be taken to avoid unnecessary heating, as continued boiling with this reagent causes a decomposition which will be spoken of presently. These needles melt at 208°. Analyses gave the following results :

---

[1] This JOURNAL, 18, 810.

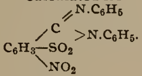
I. 0.3822 gram substance gave 0.8334 gram CO_2 and 0.1272 gram H_2O.

II. 0.2645 gram substance gave 0.5812 gram CO_2 and 0.0910 gram H_2O.

III. 0.2023 gram substance gave 0.1283 gram $BaSO_4$ (Liebig).

IV. 0.2061 gram substance gave 0.1280 gram $BaSO_4$ (Liebig).

V. 0.1853 gram substance gave 16.73 cc. N (standard).

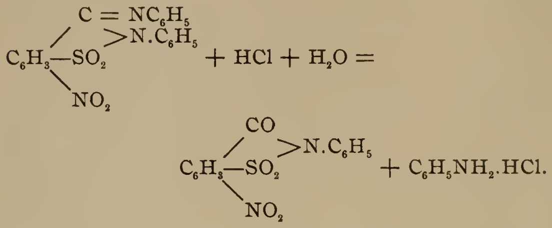
	Calculated for 	Found.				
		I.	II.	III.	IV.	V.
C	60.11	59.47	59.93	....	....	....
H	3.44	3.69	3.82	....	....	....
S	8.45	....	....	8.70	8.52	....
N	11.08	....	....	....	....	11.35

For analyses I and II, I am indebted to Mr. Nakaseko, of this laboratory, who kindly made them for me.

Action of Reagents upon the Dianil of Paranitroorthosulphobenzoic Acid.

1. *Action of Hydrochloric Acid.*—When the dianil is boiled

for some time with concentrated hydrochloric acid the yellow color of the substance disappears and the dianil is converted into a colorless substance, without, however, passing into solution. After crystallization from alcohol the substance so formed was obtained in the form of small, colorless needles. These melted at 183° and possessed all the properties of the anil, which, in fact, they proved to be. The reaction may be thus expressed :



This reaction also explains the fact that some anil was always obtained in making the dianil from the anilide. Hydrochloric acid is formed in the reaction, and in turn reacts with some of the dianil in the sense of the equation just given.

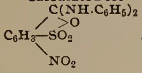
2. *Action of Alcoholic Potash.*—On boiling the dianil with alcoholic potash for a time, the solution turned red, and nothing but tarry products were obtained. In this respect the dianil differs from the dianil of orthosulphobenzoic acid which, under similar conditions, is transformed into infusible anilide. This observation is, however, in accord with the fact that the nitro derivative is in general much less stable in the presence of alkali.

3. *Action of Glacial Acetic Acid.*—When the dianil is boiled with glacial acetic acid for some time, the color of the solution changes to a much lighter shade of yellow, or disappears. On evaporating the solution to a small volume, and allowing the solution to cool, a colorless substance separates. This is the infusible anilide. It could not be obtained in crystals from any solvent, but always separated in flakes. It does not melt or undergo change at 340°. Like the fusible anilide it is soluble in alkali, but on acidifying the solution it does not at

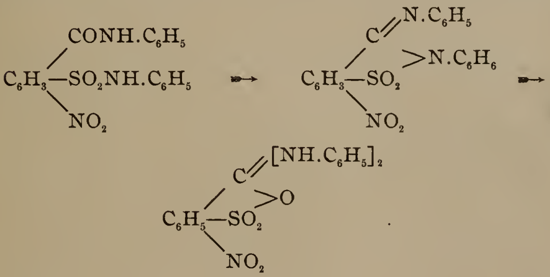
once reappear. On standing for some time, however, it gradually separates in pure form. In this particular my observation differs from that of Remsen and Gray,[1] who state that this anilide is decomposed by alkali.

A sample that had been repeatedly precipitated gave the following results on analysis :

I. 0.1607 gram substance gave 13.88 cc. N (standard).
II. 0.2195 gram substance gave 0.1285 gram $BaSO_4$.
III. 0.1357 gram substance gave 0.0807 gram $BaSO_4$.

	Calculated for  $C_6H_3(SO_2)(NO_2)C(NH.C_6H_5)_2O$	Found.		
		I.	II.	III.
N	10.58	10.85	....	....
S	8.06	....	8.00	8.16

By this series of transformations, therefore, it is possible to pass from one anilide to the other, the successive steps being :



This is of especial interest as affording a method of passing from a derivative of the symmetrical chloride to a substance derived from the unsymmetrical chloride by steps that can be clearly followed.

Conclusions.

In the course of this investigation several facts have been established :

1. By the methods described the symmetrical chloride of paranitroorthosulphobenzoic acid can be obtained in fine crys-

---

[1] This JOURNAL, 19, 496.

talline condition perfectly free from its unsymmetrical isomer, with an average yield of 40 per cent.

2. By treatment of the chloride with benzene and aluminium chloride, only one chlorine atom can be replaced by the phenyl group.

3. With alcohols the symmetrical chloride yields directly the acid ester of paranitroorthosulphobenzoic acid, no evidence of an intermediate chloroethereal salt having been observed.

4. With phenols two series of derivatives are obtained.

(*a*) With monohydroxyphenols both esters and sulphophthaleïns are formed, the former predominating.

(*b*) With polyhydroxyphenols no esters were obtained, but compounds of the unsymmetrical type, usually containing more than two phenol residues.

5. With aniline, an anil and an anilide of symmetrical constitution are formed.

6. With phosphorus oxychloride the anilide, by loss of water, forms a dianil.

7. This dianil undergoes transformation with

(*a*) Glacial acetic acid forming an anilide of unsymmetrical constitution.

(*b*) Hydrochloric acid forming the anil.

(*c*) Alcoholic potash, with the formation of colored decomposition-products.

THE COMPOSITION OF A WOOD OIL.[1]

BY G. S. FRAPS.

INTRODUCTION.

The destructive distillation of wood gives rise to a great number of compounds. The products, crude wood spirit, wood vinegar, wood creosote, wood tar, and the gases, have been the subject of frequent chemical investigation, with the result that a large number of compounds have been detected in them. Wood vinegar contains the whole series of saturated fatty acids[1,2] up to, and including caproic acid: formic acid, acetic acid, propionic acid, butyric acid, valeric acid, and caproic acid.[1] It also contains valerolactone,[3], pyrocatechol,[4] and three unsaturated acids,[2] α-crotonic acid, β-crotonic acid, and angelic acid. Wood creosote[5] is a mixture of phenols, and their acid ethers—phenol, the three cresols, the xylenols (1, 3, 4 and 1, 3, 5), orthoethylphenol, guaiacol, methylguaiacol, ethylguaiacol, propylguaiacol, and finally the dimethyl ethers of pyrogallic acid, methylpyrogallic acid, and propylpyrogallic acid. The tendency to form homologous series comes out very plainly in the list just given.

---

[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1899, for the degree of Doctor of Philosophy. The work was undertaken at the suggestion of Professor Remsen, and was carried on under his guidance.

Besides methyl alcohol and methyl acetate, the lower boiling portions of crude wood spirit contain methyl formate,[6] methyl acetate,[7] acetone, methylethylketone,[8] allyl alcohol,[9] dimethylacetal,[10] acetic aldehyde,[8] methylamine, and ethyl alcohol.[11] The presence of the last named requires confirmation, since, in spite of the fact that many chemists have worked on crude wood spirit, it has been reported but once. A still greater number of compounds have been detected in the less volatile portions of crude wood spirit; the list is a long one, and the compounds again range themselves in homologous series. We find isobutyl alcohol,[12] isoamyl alcohol,[13] and indications that higher alcohols[12] are present; methylpropylketone,[14] ketopentamethylene, or cyclopentanone or adipic ketone,[15] ketohexamethylene, or pimelic ketone,[12] and an unsaturated ring ketone, α-methyl-β-ketopentamethenylene[13] or methylcyclopentanone, C_6H_8O; toluene,[16,17] xylene,[16,17] cumene,[1,2] and cymene;[2] pyridine[3] and methylpyridine.[4]

---

[1] Barre: Compt. rend., **68**, 1222.

[2] Krämer and Grodzki: Ber. d. chem. Ges., **11**, 1356.

[3] *Ibid.*, **17**, 1369.

[4] Jahresbericht, 1864, 651.

[5] Behal and Choay: Bull. Soc. Chim. (Paris), [3] **11**, 703; Compt. rend., **118**, 1341; **119**, 166.

[6] Mabery: This Journal, **5**, 256.

[7] Völckel: Ann. Chem. (Liebig), **86**, 66.

[8] Krämer and Grodzki: Ber. d. chem. Ges., **9**, 1920.

[9] *Ibid.*, **7**, 1492.

[10] Ann. Chem. (Liebig), **132**, 240.

[11] Ber. d. chem. Ges., **13**, 661.

[12] Looft: Ber. d. chem. Ges., **27**, 1542.

[13] Wislicenus and Looft: Ann. Chem. (Liebig), **275**, 366.

[14] Vladesco: Bull. Soc. Chim. (Paris), [3], **3**, 510.

[15] Wislicenus and Hentzschel: Ann. Chem. (Liebig), **275**, 318.

[16] Krämer and Grodzki: Ber. d. chem. Ges., **9**, 1920.

[17] Cahours: Ann. Chem. (Liebig), **76**, 286.

According to E. Looft,[3] the term "wood oil" is used to designate the low-boiling portions of wood tar, and likewise the less volatile portions and residues of crude wood spirits. It is self-evident that there must be common constituents of these two products, but there may also be considerable difference.

The compounds reported as present in wood tar are: propionic aldehyde,[5] furfural[6] and methylfurfural;[7] methylfurane,[8] dimethylfurane,[5] trimethylfurane;[5] toluene,[5] xylene,[5] and cumene;[9] pyroxanthine,[10] which is a condensation-product of furfural with adipic ketone;[11] and lastly, two ketones,[12] one $C_7H_{10}O$, methylcyclohexanone; the other is still under investigation.

The above is a list of the compounds whose presence has been from time to time reported in the various liquid products from the distillation of wood. The proportions in which they are present, if they are present, is dependent upon the conditions of the distillation, the kind of wood used, etc. It is interesting to note that the list includes no mesitylene, phoron, mesityl oxide, or other compound that could justly be called a condensation-product of acetone. The statement that "condensation-products of acetone" are formed in the distillation of wood is unwarranted, though it has been made over and over again.

PART I.

INVESTIGATION OF THE WOOD OIL BOILING BELOW 140°.

The material used in this investigation is obtained from hard-wood tar. The tar is distilled, the distillate treated with caustic potash, and again distilled. The last distillate

---

[1] Cahours: Ann. Chem. (Liebig), **76**, 286.

[2] Krämer and Grodzki: Ber. d. chem. Ges., **9**, 1920.

[3] Wislicenus and Looft: Ann. Chem. (Liebig), **275**, 366.

[4] Looft: Ber. d. chem. Ges., **27**, 1542.

[5] Fischer and Laycock: Ber. d. chem. Ges., **22**, 101.

[6] Hill: *Ibid.*, **10**, 936.

[7] Hill: *Ibid.*, **22**, 607.

[8] E. Harries: *Ibid.*, **31**, 37.

[9] Volckel: Ann. Chem. (Liebig), **86**, 331.

[10] Ann. Chem. (Liebig), **21**, 43.

[11] Ber. d. chem. Ges., **29**, 1838.

[12] Behal: Compt. rend., **125**, 1036; **126**, 46.

was that received for examination. As will be seen in Part II, the treatment with alkali did not remove all acid substances. The oil was of a brownish-red color, and semitransparent. Seventeen liters of the oil were distilled, a short Hempel tube filled with glass beads being used, and fractions at intervals of 15° being collected up to 150°. To prevent the vapors from penetrating the cork stoppers, which they did at first with the greatest readiness, the corks were covered with a strong solution of sodium silicate and dried. This was a very effective way of rendering the stoppers vapor-tight.

The first distillates were cloudy. The cloudiness was removed by calcium chloride. They were subjected to a careful fractional distillation, with the same Hempel tube, collecting the fractions at intervals of 5°, except the first three, which boiled at 54° to 57°, 57° to 61.5°, 61.5° to 65°. After six fractionations, 42 per cent of the oil had passed over below 140°. The oils accumulated decidedly in the fractions 57° to 61°.5, 100° to 105°, and 130° to 135°, with another accumulation, not so marked, at 75° to 80°. The table shows the relative sizes of these fractions, expressed in percentages of the total oil.

Fraction	54°–57°	57°–61.5°	61.5°–65°	70°–75°	75°–80°
Per cent	2.3	2.6	1.3	1.2	1.7
Fraction	80°–85°	95°–100°	100°–105°	105°–110°	
Per cent	1.4	2.9	5.2	4.5	
Fraction	125°–130°	130°–135°	135°–140°	54°–140°	
Per cent	1.4	4.5	1.7	42	

The first fractions were almost colorless; in general terms, the color became darker as the boiling-point became higher, passing from colorless through light-yellow, bright-yellow to dark-yellow. The change was not regular. The color was always lighter when the oil had been freshly distilled than after it had stood for some days.

The fractional distillation above described was carried out by Mr. E. W. Magruder, to whom the thanks of the author are due.

I. SOLUBILITY.

All of the fractions were soluble in water to some extent. To determine the solubility, about 10 cc. of each fraction were shaken well in a burette with 40 cc. water, and the loss in volume measured. The high solubility of the low-boiling fractions was unexpected. The solubility decreased with increase in boiling-point of the fraction.

Fraction.	Per cent dissolved.	Fraction.	Per cent dissolved.
57°–61.5°	52	80°–85°	27
61.5°–65°	35	85°–90°	23
65°–70°	33	90°–95°	16
70°–75°	30	95°–100°	12
75°–80°	28	100°–105°	12

II. KETONES AND ALDEHYDES REMOVED BY ACID SODIUM SULPHITE.

Preliminary trials to effect combination between the oil and a solution of acid sodium sulphite were unsuccessful. It was soon found, however, that combination takes place with great readiness when a very concentrated solution of the salt is used. The solution of the acid sulphite was made by passing sulphur dioxide into a cooled solution of caustic soda (1 : 3) until the required weight was absorbed. This occurs approximately when the precipitate of sodium sulphite that first forms has redissolved. Each fraction was well shaken with a quantity of the solution so prepared, when many of them became so warm that it was thought necessary to cool with water. After standing for some time, the oil and aqueous solution were squeezed from the precipitate through a cloth, and, when the precipitate was sufficiently large, it was placed in a press and as much of the oil pressed from it as possible. The oil was treated with the solution of the sulphite a second, and in some cases a third, time.

The character of the precipitate varied with the boiling-point of the fraction from which it was separated. The more volatile oils gave crystalline precipitates easy to handle, but as the boiling temperature increased, the precipitates became more and more flocculent in character, shading into gelatinous, until those from the fractions over 120° were very like aluminium hydroxide.

From the weight of the precipitate from each fraction, dried on drying-paper in the press, the approximate weight of ketone in the corresponding fraction was calculated, making the assumption that the volume of the ketone is one-half the weight of the precipitate. Aldehydes were present with the ketones, but in such quantity as not to affect this approximation. The figures are crudely approximate, but serve to give an idea of the relative percentages of ketones in the fractions. The table shows the occurrence of the maximum percentages of ketones.

Fraction	70°–75°	75°–80°	80°–85°	95°–100°	100°–105°	105°–110°
Per cent	12	14	10	17	18	11
Fraction	110°–115°	120°–125°	125°–130°	130°–135°	57°–140°	
Per cent	3	5	18	9	mean 10	

From the above figures one might expect ketones boiling between 75°–80°, 100°–105°, 125°–130°, with the probability of one boiling below 85°. The maximum percentages of ketones are in the largest fractions in the case of fractions 75°–80° and 100°–105°. There is no accumulation of ketone in the fraction 57°–61.5°, and the highest percentage occurs in the fraction 125°–130° instead of in 130°–135°, which is three times as large. The table shows also the value of a sixfold fractional distillation with a Hempel tube, applied to a complex mixture. The separation of the ketones can hardly be called satisfactory.

(1) *Methylethylketone* (*78°*).

The sulphite compounds from the fractions boiling below 110° were distilled separately with a solution of sodium carbonate. The distillates had an aldehyde-like odor, and gave instantly a heavy mirror with ammoniacal silver oxide (Tollens' solution). With the exception of certain fractions, with which an attempt was made to identify the aldehyde, as described below, the ketones were salted out with potassium carbonate and fractionated with the others. The remainder of the sulphite compounds were decomposed with a solution of sodium carbonate under a reflux condenser and separated in the usual way. After drying all the fractions with calcium chloride they were fractionated. The distillates accumulated in the fractions 80°–85°, 100°–103°, 128°–131°, which correspond to certain ketones. The ketone boiling at 80°–85° could hardly be other than ethylmethylketone, which has been separated by Krämer and Grodzki[1] and by Vladesco[2] from crude wood spirit by means of the sulphite compound. Acetone was also present in small quantity.

(2) *Valeric Aldehyde* (*103°*).

Every ketone fraction gave the silver test for aldehydes. The aldehydes in the distillates from the sulphite compounds precipitated from the fractions 57.5°–61.5°, 85°–90°, were oxidized with ammoniacal silver oxide, and an attempt made to separate sufficient of the silver salt of the corresponding acid for analysis. This failed on account of the small quantity of aldehyde present.

Valeric aldehyde was detected in the ketone fraction 100°–103°. According to Herz,[3] ketones require many hours to be oxidized by a solution of 6 grams potassium bichromate and 8 grams sulphuric acid in 50 cc. water, even at an elevated temperature. Fraction 100°–103° became warm when shaken with this mixture. After standing a few minutes, the oil, which contained the fatty acid, was separated and distilled from potassium carbonate. The residue was distilled with dilute sulphuric acid, the distillate neutralized, silver nitrate added, and the precipitate redissolved by heating. A silver salt which had the composition of silver valerate, crystallized from the filtered solution.

0.4051 gram silver salt gave, on ignition, 0.2094 gram silver.

	Calculated for $C_5H_9O_2Ag$.	Found.
Ag	51.67	51.69

The fraction 128°–131° was treated with chromic acid in a similar manner, but while a small quantity of acid was formed it was not enough for the preparation and analysis of the silver salt. Valeric aldehyde has not before been detected in the products of the distillation of wood. While it was not possible to identify any other aldehydes in this wood oil, other aldehydes are probably present.

---

[1] Ber. d. chem. Ges., **9**, 1920.

[2] Bull. Soc. Chim. (Paris), [3], **3**, 510.

[3] Ann. Chem. (Liebig), **186**, 257.

According to Krämer and Grodzki,[1] acetic aldehyde is usually found in the most volatile distillate from crude wood spirits. Fischer and Laycock[2] report the presence of propionic aldehyde in wood tar. This gives a good basis for the belief that the process of destructive distillation of wood gives rise to an homologous series of aldehydes, corresponding to the homologous series of acids found in wood vinegar. Since acetic aldehyde, propionic aldehyde, and valeric aldehyde are already detected, corresponding to acetic acid, propionic acid, and valeric acid, one could predict that formic aldehyde, butyric aldehyde, and caproic aldehyde will be detected and fill the gaps.

(3) *Methyl-n-propylketone (102°).*

The presence of methyl-*n*-propylketone in crude wood spirits was established by Vladesco. The ketone fraction 100°–103° contains this ketone. Treated with amyl nitrite and hydrochloric acid, the fraction gave an isonitroso compound which melted at 51.5° to 52.5° after recrystallization from petroleum ether. The melting-point of the isonitroso compound of methyl-*n*-propylketone is 48° to 51°.

(4) *Adipic Ketone—Methyl-n-butylketone.*

Claisen, in 1875, separated a ketone from crude wood spirits to which he gave the formula $C_6H_{10}O$. Wislicenus and Hentzschel[3] later examined this compound, and gave it the formula C_5H_8O. They found it to be identical with the ketone formed by distilling the calcium salt of adipic acid, which yields glutaric acid by oxidation, quantitatively, and otherwise shows that it is a ring ketone—adipic ketone, or ketopentamethylene.

The ketone under examination, in the ketone fraction 128°–131°, was at first assumed to consist of adipic ketone, and confirmation was sought in the formation of the oxime. To 10 grams in a little alcohol, 4 grams hydroxylamine and a few drops of a saturated solution of sodium carbonate were added, and the mixture heated on the water-bath. The oil which separated did not solidify over night, as it was expected to do; did not solidify at all, even after long exposure to a temperature below zero. It distilled completely at 185° to 188° and still refused to solidify. Adipic oxime behaves differently. It melts at 56.5°. Adipic ketone is oxidized almost quantitatively by nitric acid to glutaric acid. The ketone in question, oxidized with nitric acid of sp. gr. 1.20 by the method of Wislicenus, yielded only one-sixth as much solid acid as it ought to yield were it pure adipic ketone. The acid formed the zinc salt characteristic of glutaric acid, more soluble in cold than in warm water.

---

[1] Ber. d. chem. Ges., **9**, 1920.

[2] *Ibid.*, **22**, 101.

[3] Ann. Chem. (Liebig), **275**, 318.

Only a portion of the fraction was adipic ketone. The other ketone present is probably methyl-*n*-butylketone (127°–128°). This is next in the series after methyl-*n*-propylketone, and its boiling-point corresponds to that of the ketone we should expect to find in the fraction of the oil 125°–130° on account of the accumulation of ketone in it. Although the fraction boiling at 130° to 135° was three times larger than that boiling at 125° to 130°, the latter contained twice as much ketone as the former. This would lead us to look for a ketone boiling between 125° and 130°. Since methyl-*n*-butylketone boils at 127° to 128°, and is the next member in the series dimethylketone, methylethylketone, methyl-*n*-propylketone, it is reasonable to suppose that the ketone in question is methyl-*n*-butylketone. Sufficient material to decide this point was not available.

(5) *Mesityl Oxide* (*130°*) (*Not Present*).

Mesityl oxide unites with acid sodium sulphite to form a compound very easily soluble in water, and easily decomposed by concentrated caustic soda to reform mesityl oxide. "Condensation-products of acetone, as mesityl oxide, phoron, etc.," have often been stated to exist in the products of the distillation of wood, but they have never been separated and described. A test for mesityl oxide in the wood oil under investigation gave negative results.

The sulphite solution which had been shaken with fraction 125°–130°, and from which all solid ketone sulphite compound had been removed, was distilled with a large excess of caustic soda. A very few drops of oil came over, which did not possess the characteristic odor of mesityl oxide. Mesityl oxide was therefore absent. The liquid in the flask assumed a deep-brown color. It was neutralized with sulphuric acid, cooled, when most of it becomes solid from the crystallized sodium sulphate, and extracted with alcohol. On evaporation, the extract left a reddish-brown, tarry mass with the odor of the oil from burning paper.

III. ETHEREAL SALTS.

The treatment with acid sodium sulphite had diminished the size of the fractions considerably, a loss perhaps due in great part to their solubility. The residues were dried with potassium carbonate and once fractionated. The distillates were colorless to yellow when freshly distilled, becoming darker on standing. As methyl formate and methyl acetate have been found in crude wood spirits, the presence of ethereal salts was suspected in the wood oil under investigation. To a few drops of different fractions in test-tubes, phenolphthalein and one drop of a very dilute solution of caustic soda were added. The red color disappeared in a few seconds, indicating ethereal salts.

The ethereal salts were saponified with an aqueous solution of caustic soda (1 : 4). Heating the oil and alkaline solution under a reflux condenser was first tried, but the operation was very slow, and other reactions than saponification took place; the solution became dark-red, and the oil itself became highly colored. Saponification in the cold by shaking the oil and solution of caustic soda together for about fifteen hours was much more satisfactory. While the alkali changed in color, the change was not so great as when heat was used. The shaking arrangement consists simply of two boards bolted to a revolving shaft and about 3 inches from it. The bottles, holding 500 cc., were held firmly in place by rawhide thongs, which passed through holes in the boards, around the bottles, and were secured by wedges in the holes. An electric motor furnished power. This simple arrangement did effective work. The oil and alkaline solution were in an emulsified condition all the time it was in motion, and the ethereal salts were rapidly and completely saponified. The bottle was placed on the shaker in the afternoon, and removed the next morning.

The oil was separated from the solution of caustic soda and measured. The loss was supposed to represent roughly the amount of ethereal salt saponified. Taking the volume of the oil that had been treated with sulphite as the basis, it varied from 80 per cent in the fraction 57.5°–61.5° to 22 per cent in the fraction 135°–140°. No attempt was made to calculate the percentage of ethereal salts in the original oil, on account of the loss due to treatment with sodium bisulphite. The percentage of ethereal salts decreases with rise in boiling-point. One might conclude from this that the quantity of organic acids in the corresponding wood vinegar decreases with increase in the boiling-point of the acid.

(1) *Alcohol—Nitriles.*

The solution of caustic soda contained the alcohol and acid of the saponified ethereal salt. It was partially distilled to remove alcohol and soluble oils. A small quantity of ammonia was always given off, possibly from the saponification of nitriles. Heusler found nitriles in coal tar.[1] The alcohol was assumed to be methyl alcohol.

(2) *Methyl Acetate (57°.3).*

The solutions of caustic soda containing the acids from the ethereal salts of the fractions 57.5°–61.5° and 61.5°–70°, were strongly acidified with dilute sulphuric acid and distilled. The crystallized silver salts prepared from the distillates gave the required percentage of silver for silver acetate.

From oil fraction 57.5°–61.5°:

0.6198 gram of the crystallized silver salt left, on ignition, 0.3983 gram silver.

	Calculated for $C_2H_3O_2Ag$.	Found.
Ag	64.66	64.26

From oil fraction 61.5°–70°.

First fractional precipitation:

0.8498 gram of the crystallized silver salt left, on ignition, 0.5435 gram silver.

---

[1] Ber. d. chem. Ges., 30, 2743.

Fourth fractional precipitation :

0.8833 gram of the crystallized silver salt left 0.5661 gram silver.

	Calculated for $C_2H_3O_2Ag$.	Found. I.	Found. IV.
Ag	64.66	63.96	64.09

Qualitative tests with iron and aluminium salts confirmed the presence of acetic acid.

Methyl acetate was first recognized in wood spirit by Völkel.[1] Together with methyl formate, which was first detected by him, it was later identified in crude wood spirits by Mabery.[2]

(3) *Methyl Propionate* (*79°.5*).

The acid distillate from fraction 70°–80° separated into two layers when treated with calcium chloride. The upper oily layer of fatty acid was lost. The acid in solution in the lower layer was distilled and the silver salt prepared from it.

First fractional precipitation :

0.3762 gram of the crystallized silver salt left, on ignition, 0.2262 gram silver.

Fifth fractional precipitation :

0.4556 gram of the crystallized silver salt gave 0.2745 gram silver.

	Calculated for $C_3H_5O_2Ag$.	Found. I.	Found. V.
Ag	59.67	60.13	60.25

While propionic acid has been separated from wood vinegar, methyl propionate has not before been detected in any distillation-products of wood.

(4) *Methyl-n-butyrate* (*102°.3*).

The fatty acids from the fractions above 80° were distilled from the acidified soda solution with steam. The clear acid distillate from fraction 95°–105° was treated with calcium chloride, and the oily layer separated. It had the disagreeable odor of the higher fatty acids. After dehydrating with calcium chloride, it distilled almost completely at 157° to 162°.

---

[1] Ann. Chem. (Liebig), 86, 66.

[2] This JOURNAL, 5, 256.

The acid, separated in the same way from fraction 105°–110°, distilled at 157° to 162° also, and was mixed with the above. The silver salt of the acid, crystallizing in needles, gave the analysis for silver butyrate.

0.5612 gram of the crystallized silver salt gave, on ignition, 0.3105 gram silver.

	Calculated for $C_4H_7O_2Ag$.	Found.
Ag	55.38	55.33

The acid separated in a similar way from fraction 110°–115° distilled from 158° to 167°. From that portion boiling at 162° to 163° the crystalline silver salt was prepared and analyzed.

0.5658 gram of the silver salt left, on ignition, 0.3116 gram silver. Per cent Ag = 55.07.

Part of the acid 157°–162° was converted into the calcium salt, and the solution partially evaporated in the cold over sulphuric acid. On heating, a copious crystalline precipitate separated, showing the presence of normal butyric acid.

A test was made for isobutyric acid in the acid boiling at 157° to 162°, the method of Victor Meyer[1] being used with a slight modification. Thirty grams acid were oxidized with an alkaline solution of potassium permanganate, the filtered liquid treated with an excess of hydrochloric acid, and neutralized with chalk, then 2 or 3 drops of ammonia added. The crystals obtained by partial evaporation of the filtered solution were decomposed with dilute hydrochloric acid, and the solution extracted with ether. The ether was evaporated, and the residue, placed in a bell-jar, over sulphuric acid, crystallized in long needles. These were so small in quantity—much less than 0.1 gram—and so deliquescent, that a melting-point determination was not made. The crystals were probably of oxyisobutyric acid. Isobutyric acid yields oxyisobutyric acid when treated as above, which is a deliquescent substance and melts at 78° to 79°. Methyl isobutyrate, if present at all, is present in minute quantity. Krämer and Grodzki tried in vain to isolate isobutyric acid from wood vinegar by fractional distillation, etc., but obtained no indications of it.

Methyl butyrate has not before been detected in wood oil, or any other distillation-product of wood.

[1] Ber. d. chem. Ges., 30, 2525. See also criticism of Erlenmeyer: *Ibid.*, 30, 2956.

(5) *Esters of Unsaturated Acids.*

The acid from fraction 115°–120° became milky when distilled. The insoluble acid was separated; the remainder was neutralized, evaporated to dryness, and distilled with sulphuric acid. The clear distillate decolorized bromine, indicating unsaturated acids.

α-Crotonic acid and β-crotonic acid have been separated from wood vinegar by Krämer and Grodzki,[1] which renders probable the presence of their methyl esters in wood oil. Methyl α-crotonate boils at 120°.7, methyl β-crotonate probably at 114° to 116°.

(6) *Methyl Valerate (127°.3).*

The distillate from each fraction above 120° had an insoluble acid floating on it. The acid was separated, dried, and distilled. The acid from fraction 120°–130° distilled mainly from 178° to 182°. Its crystallized silver salt was analyzed.

0.5868 gram silver salt left, on ignition, 0.3047 gram silver.

	Calculated for $C_5H_9O_2Ag$.	Found.
Ag	51.67	51.94

The silver salt from the acid from fraction 130°–135°, boiling at 184° to 188°, also gave results for silver valerate.

First precipitation:

0.3892 gram of the crystallized silver salt left, on ignition, 0.2010 gram silver.

Fifth precipitation:

0.5302 gram of the crystallized silver salt gave, on ignition, 0.2745 gram silver.

	Calculated for $C_5H_9O_2Ag$.	Found.	
		I.	V.
Ag	51.67	51.67	51.77

The calcium and zinc salts of the acid boiling at 184° to 188° were more soluble in cold than in hot water, indicating normal valeric acid. Methyl valerate has not before been detected in any products of the distillation of wood.

(7) *Esters of Other Acids.*

The acid which floated on the surface of the distillate from fraction 135°–140° distilled at 189° to 194°, and analysis of its silver salt pointed to the presence of esters of organic acids with a higher molecular weight than valeric acid.

---

[1] Ber. d. chem. Ges., **11**, 1356.

0.5213 gram of the crystallized silver salt left, on ignition, 0.2654 gram silver.

	Calculated for $C_5H_9O_2Ag$.	 $C_6H_{11}O_2Ag$.	Found.
Ag	51.67	48.43	50.91

Besides the volatile acids already described, the caustic soda solutions contained a small quantity of a very dark acid, which remained suspended in the acidified liquid after the other had been distilled off.

IV. OTHER KETONES.

The oils undissolved by the sodium hydroxide were dried and fractionated. The distillates reacted with phenylhydrazine, showing keto bodies still present. Phenylhydrazine was added to all the fractions above 85°, when action took place with evolution of heat and separation of water. After standing over night the excess of phenylhydrazine was removed with acetic acid, and the uncombined oil distilled with steam. Treatment with phenylhydrazine, etc., was repeated. The loss of the oil treated with sodium hydroxide in this operation averaged 24 per cent, greatest with fraction 105°–110°, least with fraction 135°–140°, with another maximum at fraction 115°–135°.

The phenylhydrazine compound remaining in the flask after the oil had been distilled was decomposed with concentrated hydrochloric acid, and the ketone distilled with steam. The distillate was unexpectedly small. It united in part with acid sodium sulphite. That which did not unite was dried with calcium chloride and distilled. It had the agreeable odor of ketones.

Ketone from fraction 85°–105° distilled for the most part at 98° to 101°, probably being diethylketone (103°).

Ketone from fraction 115°–135° distilled mostly at 118° to 122°.

Ketone from fraction 135°–140° distilled all the way from 130° to 140°.

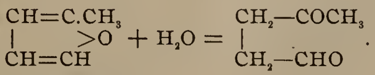
The quantity of these distillates was not sufficiently large to justify further examination.

V. ABSENCE OF ALCOHOLS AND PYRIDINES.

After the removal of ketones from a wood spirit residue, Wislicenus and Looft[1] had left a liquid which reacted readily with acetic anhydride and acetyl chloride, and contained alcohols and pyridines. It was natural to suppose that the wood oil under investigation would have some resemblance to the product just named, and that the residue left after ethereal salts and ketones had been removed would contain alcohols and pyridines. Such was not the case, however. The residue did not react with phosphorus trichloride or with acetyl chloride, nor was there any indication of pyridines at any stage of the investigation, not even the odor. Other facts showed clearly that the wood oil under investigation differed materially from the wood spirit residue examined by the investigators named. Whether this difference is due to the method of distillation of the wood, or to the one being a "wood oil" from crude wood spirits, and the other a "wood oil" from wood tar, is an open question, but I am more inclined to the latter opinion.

VI. METHYLFURANE—DIMETHYLACETAL.

Atterberg[2] isolated a body C_5H_6O from the tar of *Pinus sylvestris*, which he recognized to be methylfurane. He named it sylvane. C. Harries[3] has recently separated the same body from beech-wood tar. The residue left from the tar boiling below 70°, after washing with sodium bisulphite and with caustic soda, fractional distillation and purification with sodium, yielded a chief fraction boiling at 65°, which proved to be almost pure sylvane. It was hydrolyzed to the aldehyde of levulinic acid, which showed it to be α-methylfurane.



$$\begin{array}{l} CH{=}C.CH_3 \\ | \qquad\quad >O \\ CH{=}CH \end{array} + H_2O = \begin{array}{l} CH_2{-}COCH_3 \\ | \\ CH_2{-}CHO \end{array} .$$

---

[1] Ann. Chem. (Liebig), **275**, 366.

[2] Ber. d. chem. Ges., **13**, 879.

[3] *Ibid.*, **31**, 37.

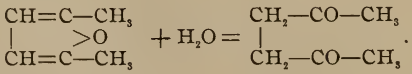
Sylvane was present in the wood oil under investigation. The fraction 64°–70°, which had not been subjected to the action of phenylhydrazine, was treated with sodium and distilled after action had ceased. The colorless distillate soon became colored in the air. Heated with dilute hydrochloric acid in a sealed tube it formed a heavy oil, which gave the pyrrol reaction.

Proceeding in the manner described above—that is, treating with sodium bisulphite, sodium, etc., Roscoe and Dancer[1] isolated a compound with almost the same boiling-point (63°) as sylvane, from crude wood spirits, which, from analysis and the vapor density, they decided to be dimethylacetal. Considering that aldehydes and methyl alcohols come together at a high temperature during the distillation of wood, one might expect to find dimethylacetal as well as derivatives of higher aldehydes. Krämer and Grodzki state that dimethylacetal is a constant constituent of crude wood spirits. Mabery was unable to detect it in the crude wood spirits examined by him. Dimethylacetal might easily be present in the sylvane from wood tar, but a test proved that the one under investigation contained none.

Eleven cc. sylvane were poured through the tube of a condenser upon phosphorus iodide (from 44 grams iodine and 8 grams phosphorus). Reaction took place with evolution of heat. After heating for five minutes on the water-bath, the condenser was turned down, and an attempt made to distil off the product, but not a single drop came over, even after heating for half an hour. Dimethylacetal would have produced methyl iodide, volatile at 45°.

VII. OTHER FURANES.

Paal and Dietrich[2] have pointed out that very dilute aqueous hydrochloric acid at 170° hydrolyzes dimethylfurane to acetonylacetone:



$$\begin{array}{l} CH{=}C{-}CH_3 \\ | \qquad >O \\ CH{=}C{-}CH_3 \end{array} + H_2O = \begin{array}{l} CH_2{-}CO{-}CH_3 \\ | \\ CH_2{-}CO{-}CH_3 \end{array} .$$

---

[1] Ann. Chem. (Liebig), **132**, 240.

[2] Ber. d. chem. Ges., **20**, 1085.

E. Fischer and Laycock[1] applied this method to the examination of a sugar oil. The fraction boiling about 94°, heated six hours at 170°, in a sealed tube with dilute hydrochloric acid, allowed acetonylacetone to be salted out with potassium carbonate from the acid solution; later Laycock[2] examined the oil boiling at about 115°, and obtained methylacetonylacetone. In the former investigation, Fischer and Laycock applied the method to a wood tar,[3] also. They say, "From the fraction 85°–100° by decomposition with dilute hydrochloric acid, we obtained a diketone which, in all probability is acetonylacetone. The fraction 100°–120°, treated in the same manner, gave a ketone which, from the analysis and the melting-point of the phenylhydrazine compound, seems to be the next homologue of acetonylacetone." This proves that dimethylfurane and trimethylfurane are present in the wood tar.

The oil unacted on by phenylhydrazine was dried and distilled. All aldehydes, ketones, and ethereal salts had now been removed. The distillates, colorless when fresh, rapidly become colored, assuming a yellow or dark-yellow color. A preliminary experiment, heating samples of the oil in sealed tubes with dilute hydrochloric acid, showed the presence of furanes, as the oil salted out by potassium carbonate from the hydrochloric acid solution gave the pyrrol reaction. As considerable quantities of material were to be treated with hydrochloric acid to remove furanes, heating in sealed tubes with dilute hydrochloric acid did not commend itself. It was found that the furane could be hydrolyzed by strong hydrochloric acid in the cold, with satisfactory results. The oil was shaken for fifteen hours with hydrochloric acid (2 vols. HCl, 1.175 sp. gr., to 1 vol. H_2O), on the shaker used for hydrolyzing the ethereal salts. The acid solution was neutralized with sodium carbonate, and the ketone in it salted out with potassium carbonate. The loss in volume of the oil was considered to represent the relative quantity of furanes hydrolyzed; it decreased regularly, and in the oils freed from ketones and ethereal salts, varied from 66 per cent in fraction 85°–95° to 10 per cent in 130°–140°.

---

[1] Ber. d. chem. Ges., **22**, 101.

[2] *Ibid.*, **10**, 1358.

[3] Ann. Chem. (Liebig), **258**, 230.

(1) *Dimethylfurane.*

Fractions 85°–95° and 95°–105° together yielded about 14 cc. ketone boiling at 187° to 193°, mainly at 191° to 192°. Eleven grams of this with 12 grams hydroxylamine and 13 grams sodium carbonate in 30 cc. water, gave a precipitate of 10 grams oxime. Recrystallized from water, its melting-point (134°), and analysis proved it to be the dioxime of acetonylacetone.

0.3556 gram substance yielded 55.21 cc. nitrogen under standard conditions.

	Calculated for $CH_3C.(N.OH)C_2H_4C.(N.OH)CH_3$.	Found.
N	19.37	19.48

Acetonylacetone was produced by the hydrolysis of dimethylfurane.

(2) *Trimethylfurane.*

The ketone produced by the hydrolysis of fraction 115°–130° distilled at 199° to 202°, mainly at 200° to 201°. The dioxime prepared as above melted at 128° to 129° after it was recrystallized from water. Analysis and melting-point confirmed the belief that it was the dioxime of methylacetonylacetone.

0.1832 gram substance yielded 25.8 cc. nitrogen under standard conditions.

	Calculated for $C_7H_{12}(NOH)_2$.	Found.
N	17.72	17.67

Methylacetonylacetone was produced by the hydrolysis of trimethylfurane.

VIII. UNSATURATED COMPOUNDS.

The dark-colored oils remaining undissolved after treatment with hydrochloric acid were dried with potassium carbonate and distilled. Addition of hydrochloric acid had taken place, and perhaps condensation reactions also, as they contained substances which boiled much higher than the original oil. Each fraction was distilled to a temperature 10° to 15° above its previous boiling-point. The distillates are described below. The residue varied from 56 per cent of the fraction 85°–95° to 4 per cent of fraction 140°–145°, showing that the quantity of compounds affected by hydrochloric acid decreases with the boiling-point. The boiling-point of the residue from fraction 85°–95° went above the range of the thermometer. The residues gave a heavy precipitate when boiled with alcoholic silver nitrate, showing the addition of hydrochloric acid. Unsaturated compounds which add hydrochloric acid are present in quantities that decrease as the boiling-point rises.

The distillates were subjected to three fractional distillations. They accumulated in the fractions boiling at 108° to 112° and 137° to 140°.

Concentrated sulphuric acid acted slightly on all the fractions, becoming yellow, and more decidedly on fraction 115°–118°. In the latter case oil and acid both became red-brown. Bromine in carbon disulphide was decolorized rapidly by all the fractions, with no hydrochloric acid fumes evolved at first; after standing a short time, hydrobromic acid was given off, the liquid became brown, and a brown oil separated. These reactions evidently indicate unsaturated compounds. The fractions 108°–112° and 137°–140° consisted for the most part of aromatic hydrocarbons, but they contained a body which gave with nitric acid a bright-red coloration, which quickly disappeared.

IX. AROMATIC HYDROCARBONS.

Toluene and metaxylene, cumene and cymene have been detected in wood tar. The chief fractions 108°–112° and 137°–140° correspond to the first two hydrocarbons.

Twenty grams of fractions 108°–112° treated with nitric and sulphuric acids yielded 30 grams of the nitro compound. This crystallized from alcohol in long needles, which melted at 70°, and is dinitrotoluene. At least 75 per cent of fraction 108°–112° was toluene.

Twenty grams of fraction 137°–140° yielded 30 grams of a nitro compound, difficultly soluble in alcohol, and crystallizing from benzene in needles which melted at 180°.5 (uncorr.), and is trinitro-*m*-xylene. At least 65 per cent of fraction 137°–140° was *m*-xylene.

X. SUMMARY OF RESULTS.

The following is a summary of the results reached in the first part of this investigation :

- Wood oil.
  - *Removed by Sodium Bisulphite :*
    - Aldehydes.
      - Valeric aldehyde.
    - Ketones.
      - Acetone.
      - Methylethylketone.
      - Methylpropylketone.
      - Methylbutylketone.
      - Adipic ketone.
- *Residue.*
  - *Removed by Caustic Soda :*
    - Nitriles.
    - Ethereal salts.
      - Methyl acetate.
      - Methyl propionate.
      - Methyl *n*-butyrate.
      - Methyl *n*-valerate.
      - Esters of unsaturated acids.
- *Residue.*
  - Sylvane.
  - *Removed by Phenylhydrazine :*
    - Ketones.
      - Diethylketone.
- *Residue.*
  - *Removed by Hydrochloric Acid :*
    - Furanes.
      - Dimethylfurane.
      - Trimethylfurane.
- *Residue.*
  - Distillation :
    - *Volatile :*
      - Unsaturated compounds.
      - Aromatic hydrocarbons.
        - Toluene.
        - *m*-Xylene.

Residue.

Hydrochloric acid addition-products.
Polymerized compounds.

PART II.

INVESTIGATION OF THE WOOD OIL BOILING ABOVE 140°.

As shown in the preceding pages, the wood-oil boiling below 140° consists of an homologous series of aldehydes, ketones, furanes, ethereal salts, aromatic hydrocarbons, and unsaturated compounds whose nature was not determined. The wood oil boiling above 140° has been little investigated. Several ketones, indications of higher alcohols, cumene, cymene, furfural, methylfurfural, and methylpyridine have been found in it from time to time, but the composition of the greater portion of the oil is still unknown. It was hoped to extend the homologous series found in the lower-boiling oils into the higher fractions, and perhaps find new series. The investigation was not carried far, however.

The oil left after distilling off the portion boiling below 140°, about 7.5 liters, was fractionated three times without a Hempel tube. The distillation was attended with slight decomposition and continuous elimination of a small quantity of water, especially noticeable when the distillation was discontinued and renewed. Krämer and Grodzki observed the same phenomenon. The decomposition became very marked at 195° to 200°, and the first distillation was stopped at 200°. The two succeeding fractionations were carried to 210°. Only one chief fraction, boiling at 165° to 170°, appeared, little different in size, however, from those boiling at 155° to 160°, 160° to 165°, and 170° to 175°. These four fractions contained 45 per cent of the distillate between 140° and 210°. Other fractions diminished regularly on each side.

I. ALDEHYDES—KETONES.

Fractions boiling over 180° gave no precipitate with sodium bisulphite, and with the lower boiling fractions the quantity was small. The distillates from the sulphite compounds, decomposed with sodium carbonate, gave the silver mirror, but the quantity of aldehydes was too small to allow their identification. Fraction 155°–160° and the distillate from the sulphite compound from fraction 150°–155° gave the red color with aniline acetate, which indicates furfural. Not sufficient of it was present to respond to a more decisive test.

The dried ketones were once fractionated. The chief fraction boiled at 145° to 150°, with small quantities boiling up to 185°. Pimelic ketone or cyclohexanone (153°), separated by Looft from crude wood spirits residue, was expected to be present. It yields adipic acid on oxidation with nitric acid. Ketone fraction 150°–155 oxidized with nitric acid 1.2 sp. gr. left a solid acid on evaporation, which crystallized from water in thin leaves melting at 95°. Adipic acid melts at 148°. There was not sufficient of the acid for further examination.

Looft separated an unsaturated ketone, β-methylketopentamethenylene or methylcyclopentanone from the residue of crude wood spirits by means of the oxime. It boils at 157°, and unites easily with acid sodium sulphite to form a compound very soluble in water, not decomposed by alkalies or alkaline carbonates, but decomposed by hydrochloric acid. This ketone appears to be absent from the wood oil here examined, or, if present, only in minute quantities. To test for it, the sulphite residue and compound from the fractions 145°–150° and 150°–155° were distilled with sodium carbonate to remove all other ketones, then distilled with a large excess of hydrochloric acid. A few drops of oil came over, with the odor of fatty acids, and almost all of it dissolved in sodium carbonate.

II. ETHEREAL SALTS—CREOSOTE.

Like the ketones, ethereal salts were present in very small quantity. They were saponified as in Part I, and the loss of oil at first considered to represent the quantity of ethereal salts removed, but most of the loss in the fractions boiling above 150° was later found due to the presence of creosote, not ethereal salts. The percentage of loss in the oil washed with sulphite solution decreased from 18 per cent in fraction 135°–140° to 4 per cent in fraction 145°–150°, then increased regularly up to 45 per cent in fraction 205°–210°. The increase was caused by increasing amounts of creosote. The acids separated from the solution of caustic soda were dried and once fractionated. The distillates were found to contain phenols. They were dissolved, in three portions, in a solution of caustic soda; the phenols liberated by saturating with carbon dioxide, separated, and the solution extracted with ether. The phenols were not further examined.

The purified acids were liberated with sulphuric acid, separated, dried, and once fractionated. All the fractions were small. The distillates were colorless up to 210°, then slightly yellow, and all had the odor of the monobasic fatty acids. A small quantity of solid acid separated from fractions 225°–235°, which was not further examined. The largest fraction was the one boiling from 195° to 200°. Its silver salt was prepared and analyzed.

0.3777 gram of the silver salt left, on ignition, 0.1892 gram silver.

	Calculated for		
	$C_5H_9O_2.Ag$.	$C_6H_{11}O_2Ag$.	Found.
Ag	51.67	48.43	50.09

The acid was plainly a mixture. A little potassium carbonate was added to it, and the acid distilled off. The silver salt from the residue approached the composition of silver valerate. One would expect the acid of higher molecular weight to remain combined with the potash but this was not the case.

0.9509 gram of the silver salt left, on ignition, 0.4872 gram Ag.

	Calculated for $C_5H_9O_2Ag$.	Found.
Ag	51.67	51.23

The acid is a mixture of valeric and caproic acids.

Methyl *n*-valerate was found in the oil which distilled below 140°. It appears that methyl caproate is also present.

Fraction 220°–225° of the acid also appears to be a mixture. The silver salt gave the following analysis:

0.5915 gram silver salt left, on ignition, 0.2760 gram silver.

	Calculated for		
	$C_6H_{11}O_2Ag$.	$C_7H_{13}O_2Ag$.	Found.
Ag	48.43	45.57	46.66

The acid is perhaps a mixture of caproic and heptoic acids, and methyl heptoate is present in wood oil. Small quantities of the fatty acids distilled above 225°, but they could not be examined. According to this, acids of higher molecular weight than caproic acid will be found in wood vinegar.

III. FURANES—UNSATURATED COMPOUNDS.

A very small percentage of the oil consists of furanes. Shaken with hydrochloric acid (fractions 150°–155°, 160°–165°, 170°–175° tried), it becomes very dark and a small part dissolves. Oils could be salted out from the solutions, which appear to be diketones. Furanes higher than trimethylfuranes are present, and make up a very small fraction of the oil.

The very dark oil separated from the concentrated hydrochloric acid had undergone a change, by addition of hydrochloric acid, and perhaps polymerization. Fraction 150°–155°, treated with hydrochloric acid and dried with potassium carbonate, when distilled, began to decompose with formation of hydrochloric acid when the temperature passed beyond 155°. That portion of it which distilled at 175° to 180°, after having been well washed with sodium carbonate and water, gave a copious precipitate of silver chloride when heated with alcoholic silver nitrate. The compounds which take up hydrochloric acid or are polymerized or decomposed by it, make up a considerable proportion of the wood oil.

IV. PHENOL ETHERS.

Since, in the distillation of wood, phenols and methyl alcohol come together at high temperatures, and at th emoment of formation one might reasonably expect to find neutral phenol ethers in the products. Wood-tar creosote consists of monophenols and the acid methyl ethers of di- and tri-acid phenols, which also would lead one to look for neutral methyl ethers in the distillation-products of wood.

Forty cc. of fraction 150°–155°, previously treated with hydrochloric acid, and forty cc. of fraction 175°–180°, were heated with 30 cc. concentrated hydrochloric acid in sealed tubes for five and a half hours at 175° to 180°. On opening the cold tubes gas escaped with effervescence, which burned with a beautiful dark-green flame (methyl chloride). The acid solutions were separated, made alkaline with potassium carbonate, and distilled with steam. Both distillates gave precipitates with bromine water, but neither would give the color reaction with ferric chloride. Distillate from fraction 175°–180°, however, had the unmistakable odor of cresol, and I therefore, consider that this test shows the probable presence of minute quantities of neutral phenol ethers in the wood oil.

Tiemann and Kopp[1] separated an indifferent oil from wood tar creosote, which, from determination of the vapor-density of the different fractions, they decided to be a mixture of neutral phenol ethers with hydrocarbons. Their oil boiled above 205°; and methylphenyl ether (155°) and the methyl cresol ethers, could not have been contained in it.

V. CERTAIN REACTIONS.

The work just described shows that the wood oil boiling above 140° contains creosote, and very small percentages of aldehydes, ketones, furanes, ethereal salts, and phenol ethers. The remainder of the oil contains, in all probability, the aromatic hydrocarbons cumene and cymene, as well as large quantities of unsaturated compounds and other bodies of unknown nature. It was not thought profitable to separate the aromatic hydrocarbons, and investigation of the unknown portion was not inviting, considering the time and quantity of material then available. Beyond certain reactions which afford possible points of attack, the research was not carried further.

Acetyl chloride and phosphorus trichloride gave no indications of alcohols. Potassium permanganate oxidized the oils with great energy, but not completely.

Concentrated sulphuric acid dissolves part of the oil with heat, and the acid becomes very dark. The undissolved oil has an aromatic odor and consists, for the most part, of aromatic hydrocarbons. The aromatic hydrocarbons were separated by previous investigators in this manner. When the acid is poured into water, a dark-brown oil separates, which possesses an agreeable odor. An oil separated by Völckel[1] in a similar manner from beech-wood tar gave on analysis (from tar fraction 140°–150°) :

---

[1] Ber. d. chem. Ges., 14, 2005.

C	75.11
H	10.38
O	14.51

The oil had been purified by distillation with steam.

Bromine is absorbed with the greatest avidity. If the product is distilled with water vapor, an oil lighter than water passes over, then an oil heavier than water, and a black tar remains behind. If an attempt is made to distil the oil heavier than water by itself, it decomposes.

Glacial acetic acid allows the wood oil to be separated into two portions, one soluble, the other insoluble or soluble with great difficulty. For example, 100 grams glacial acetic acid dissolved 6 cc. from 50 cc. of the fraction 160°–165°, plus 40 cc. from 380 cc. of the same fraction. The acetic acid solution took up bromine without evolution of hydrobromic acid, and a heavy oil separated when the product was poured into water. The product was distilled with steam ; a heavy oil first passed over, then a yellow solid crystallizing in long needles comes over very slowly. There was not enough of the latter to recrystallize. The oil turned red when heated above 100° and gave off acid fumes. It then quickly became black, and began to distil at 180°, with considerable decomposition.

The acetic acid solution yields a solid, crystalline precipitate when shaken with water and potassium nitrite.

SUMMARY AND CONCLUSIONS.

The following are the results of this research :

(1) The wood oil examined is a mixture of homologous series of different classes of compounds.

(2) It probably contains the series of aldehydes $C_nH_{2n}O$, corresponding to the series of saturated acids $C_nH_{2n}O_2$, found in wood vinegar, which goes up to and includes caproic acid. The quantity of aldehydes is so small that only one could be positively identified, valeric aldehyde. Acetic aldehyde and propionic aldehyde have been found in wood oil by other in-

---

[1] Ann. Chem. (Liebig), 86, 331.

vestigators, and these facts justify the first statement. It contains furfural in minute quantity.

(3) It contains the series of ketones $C_nH_{2n}O$, of which dimethylketone, methylethylketone, methylpropylketone, and probably methyl-*n*-butylketone and diethylketone have been detected.

(4) It contains the ring ketone, cyclopentanone, and other ring ketones.

(5) It contains no mesityl oxide nor methylcyclopentanone.

(6) It contains nitriles in minute quantity.

(7) It contains the methyl esters of the saturated acids, $C_nH_{2n}O_2$, found in wood vinegar, including methyl acetate, methyl propionate, methyl *n*-butyrate, methyl *n*-valerate, very probably methyl caproate, and methyl heptoate and possibly methyl isobutyrate. The acid corresponding to methyl heptoate has not yet been found in wood vinegar. The percentage of ethereal salts decreases as their boiling-points rise, the lower-boiling ones being present in considerable quantity, the higher ones in very small quantity. One might conclude from this that the quantity of the corresponding acids in wood vinegar decreases with increase in boiling-point.

(8) It contains the esters of unsaturated acids.

(9) It contains methylfurane, and furanes which can be hydrolyzed by cold, strong hydrochloric acid to diketones. The furanes include dimethylfurane, trimethylfurane, and higher furanes.

(10) It contains no dimethylacetal, nor appreciable quantities of pyridines or alcohols.

(11) It contains compounds which take up hydrochloric acid and bromine, and are therefore unsaturated.

(12) It contains the aromatic hydrocarbons, toluene and xylene, and probably cumene and cymene.

(13) It contains creosote.

(14) It contains phenol ethers in minute quantity.

(15) The higher boiling oils, freed from ketones, aldehydes, ethereal salts, and creosote can be separated into two parts by glacial acetic acid, the one soluble in that substance, the other insoluble. Both absorb bromine readily.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXVII.—ON TRIPHENYLCHLORMETHANE.

By James F. Norris and Warren W. Sanders.

In a study of the application of the Friedel and Crafts reaction to halogen compounds in which the halogen is not joined to carbon, an account of which will be given in a subsequent paper, it was found that under certain conditions condensation-products could be isolated, the preparation of which, by the usual method of procedure, was impossible. For example, when phenyliodide dichloride and benzene were used, one of the chlorine atoms was replaced by phenyl and diphenyliodonium chloride was formed. As the method of carrying out the reaction is different from that which is usually employed in condensations with aluminium chloride, it seemed possible that a study of some carbon compounds under the conditions used in preparing the iodonium chloride, might lead to interesting results.

Carbon tetrachloride was first investigated. This reaction had been previously studied by Friedel and Crafts and by E. and O. Fischer with the result that triphenylmethane and not tetraphenylmethane was obtained. On account of this fact the study of this compound seemed of especial interest. As the result of the reaction we obtained triphenylchlormethane.

An account of this work was about to be sent to the editor of this Journal, when the paper by Gomberg,[1] describing the study of this reaction, appeared. Our results are essentially those of Gomberg, but the procedure used by us is somewhat different. The yield of the pure reaction-product which has been obtained is greater, and, further, we have succeeded in isolating a crystalline intermediate product containing aluminium, which has a bearing on the recently published explanation of the mechanism of the Friedel and Crafts reaction.

Gomberg[2] has also reported a study of the action of metals on triphenylchlormethane and has obtained an unusually interesting substance, which is considered to be the free radical triphenylmethyl, $(C_6H_5)_3C$—. He wishes to reserve this field for further work. As we have been working with triphenylchlormethane in this laboratory for about a year, with the view of preparing tetraphenylmethane from it, it seems advisable to give a preliminary account of the work that has been accomplished, and to describe briefly what is now in progress.

---

[1] J. Am. Chem. Soc., **22**, 752.

[2] *Ibid.*, **22**, 757.

The method of carrying out the Friedel and Crafts reaction, which we have found to give excellent results, consists, in brief, in adding aluminium chloride to a mixture of the theoretical quantities of the halogen compound and the hydrocarbon dissolved in a comparatively large quantity of carbon disulphide, care being taken to prevent a rise in temperature during the reaction. The flask containing the mixture is placed in ice-water, which slowly comes to the room temperature. The reaction is allowed to proceed for from twelve to forty-eight hours. When carbon tetrachloride and benzene were brought together under these conditions, a reaction took place slowly, and at the end of a few hours a heavy, dark-brown oil had separated. At the end of three days' crystals were seen in the oil, which changed, on standing, into a solid mass of crystals cemented together by a dark, amorphous substance.

These crystals decomposed rapidly when brought into contact with the air. They were insoluble in benzene, carbon disulphide, carbon tetrachloride, and petroleum ether. They were decomposed by alcohol, ether, acetone, chloroform, and acetic acid, but were soluble in nitrobenzene without decomposition. The compound was recrystallized from a mixture of nitrobenzene and carbon disulphide, and was obtained in the form of brown monoclinic prisms, terminated by basal planes, and modified by orthopinacoids. In one experiment crystals one-half inch in length were formed. The compound was found on analysis to have the composition represented by the formula $Al_2Cl_6.2(C_6H_5)_3C.Cl$.

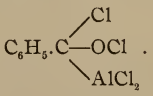
When these crystals, or better the heavy oil from which the crystals separate, are treated with ice, the compound is broken up, and triphenylchlormethane is formed. By proceeding with care, 97 per cent of the theoretical yield was obtained. Hemilian,[1] who prepared the chloride from triphenylcarbinol and phosphorus pentachloride, gives 105°–115° as its melting-point. We prepared samples of the chloride, by crystallizing it from a mixture of carbon disulphide and petroleum ether, which melted at 108°–111°. Recrystallization did not change the melting-point. Gomberg found that the substance melts usually at 108° to 112°. As triphenylchlormethane is readily converted into triphenylcarbinol by the action of water, the preparation of the carbinol is best effected by this reaction.

---

[1] Ber. d. chem. Ges., 7, 1203.

The formation of an addition-product of aluminum chloride and triphenylchlormethane is in accord with the explanation of the mechanism of the Friedel and Crafts reaction which has been put forward by Boeseken.[1] In studying the condensation of acid chlorides and hydrocarbons by this reaction it was found that a compound of the organic and inorganic chloride is first formed; that this compound reacts with the hydrocarbon with the evolution of hydrogen chloride; that an addition-product of the resulting ketone and aluminum chloride is then formed; and that, finally, this compound is broken down by water and the ketone is set free. In view of these facts an effort was made to prepare a compound of carbon tetrachloride and aluminum chloride to discover if the above explanation could be applied in full to this particular case. No such compound could be isolated.

In a recent paper Kronberg[2] has suggested that the formation of addition-products of aluminum chloride and acid chlorides is due to the fact that acid chlorides contain a carbonyl group. The structure assigned to the compound containing benzoyl chloride, for example, is as follows:



The nature of the compound containing triphenylchlormethane cannot be explained in this way. In view of this and the fact that Kohler[3] has shown that these addition-products of acid chlorides and aluminium chloride have double the molecular weight which has been assigned to them, for example the above compound has the formula $Al_2Cl_6.2C_6H_5COCl$, it seems that the suggestion of Kronberg does not explain the facts. The structure of the compound of aluminium chloride and triphenylchlormethane is best explained by giving to it a formula analogous to those proposed by Remsen[1] for the inorganic double chlorides. The compound is of interest as it is the first addition-product of aluminium chloride and an alkyl halide that has been described.

---

[1] Rec. trav. chim. Pays-Bas., **19**, 19.

[2] J. prakt. Chem. [2], **61**, 494.

[3] This JOURNAL, **24**, 385.

The isolation of a compound of aluminium chloride and triphenylchlormethane furnishes what appears to be a probable explanation of the non-formation of tetraphenylmethane from carbon tetrachloride. The double compound is readily formed from its constituents and is insoluble in benzene and carbon disulphide. Consequently, during the course of the reaction, as soon as three chlorine atoms have been replaced by phenyl groups, addition takes place, and the compound is precipitated and thus removed from further action. The opinion has been put forward that the non-formation of tetraphenylmethane by this reaction is due to the fact that there is not sufficient room for four phenyl radicals to be grouped about one carbon atom. It seems probable, in view of the facts as now known, that this stereochemical explanation is gratuitous.

Some time ago Gomberg[2] described a method of preparing tetraphenylmethane. As less than 0.5 gram of the substance was obtained in the first investigation, and a careful revision of the work[3] did not lead to a better yield, it seemed of importance to attempt to prepare the hydrocarbon by another reaction. A number of chemists have endeavored to obtain this compound. Most of the usual synthetical methods have been studied, but in no case was tetraphenylmethane obtained. As we had worked out a method of preparing triphenylchlormethane readily, we attempted to condense it with brombenzene by means of sodium. This application of the Fittig synthesis—apparently the most direct method of preparing the hydrocarbon—had not been studied, no doubt for the reason that Elbs[1] and others had found that triphenylbrommethane is not acted upon by sodium. Anschütz[2] endeavored to condense triphenylbrommethane and benzyl chloride and obtained as the result of the reaction dibenzyl and unchanged triphenylbrommethane. We, nevertheless, studied this reaction, thinking that with brombenzene a condensation might result, as it is known that a mixture of a halogen derivative of an aromatic hydrocarbon and an alkyl halide condense more readily than two alkyl halides. In other words, that a Fittig synthesis is possible at times when a Wurtz synthesis fails. In the experiment of Anschütz two halogen derivatives of methane were used.

---

[1] This JOURNAL, 11, 291.

[2] Ber. d. chem. Ges., 30, 2043.

[3] J. Am. Chem. Soc., 20, 773.

As the formation of three compounds is possible in a synthesis of this kind involving two different halogen compounds, we subjected triphenylchlormethane, dissolved in ether, to the action of sodium under the same conditions of concentration and temperature which were used when brombenzene was present, in order to make ourselves sure that hexaphenylethane was not formed. The solution of the halogen compound was allowed to stand two weeks in contact with sodium, and finally was heated to boiling for an hour. As no change was apparent, the ethereal solution was decanted and evaporated to crystallization. The compound obtained was shown to be triphenylchlormethane.

To a mixture of triphenylchlormethane, ether, and sodium, identical with the above and prepared at the same time from the same reagents, brombenzene was added. In this case a reaction took place. The ether soon assumed a light-brown color and a powder separated. The reaction was complete in about three days. The ethereal solution was decanted from the insoluble reaction mixture, and yielded, on evaporation, diphenyl. The amount obtained corresponded to about one-half of the brombenzene used in the experiment. The reaction-product which separated from the ether was found to be a mixture. One of the constituents of this mixture was obtained in crystalline condition and was analyzed. The crystals were shown not to contain halogen, yet on analysis the carbon and hydrogen did not add up to 100 per cent. We made a number of analyses, thinking that our work was at fault, but repeated effort gave practically the same results. This compound resembles closely in melting-point, chemical composition, and solubility the substance obtained by Gomberg when triphenylchlormethane was treated with zinc. Gomberg expected the formation of a hydrocarbon, but, as in our case, repeated analyses finally proved that the substance was an oxygen compound. Gomberg has come to the conclusion that the substance is a peroxide of the formula

---

[1] Ber. d. chem. Ges., **17**, 700.

[2] Ann. Chem. (Liebig), **235**, 226.

$$(C_6H_5)_3C—O—O—C(C_6H_5)_3,$$

and that it is the result of the action of oxygen on the free radical $(C_6H_5)_3C—$, which is first formed when triphenylchlormethane is treated with zinc. The compound isolated by us resembles closely this peroxide, but further work is necessary before the identity of the two substances can be established.

We had reached this stage in our work, when the close of the school-year made it necessary to postpone the further investigation of the subject. We propose to study carefully the action of sodium on a mixture of triphenylchlormethane and brombenzene, and to isolate if possible the other products of the reaction The work which is being carried on at present, and which is to be continued, has for its ultimate aim the preparation of tetraphenylmethane. While it has a bearing on the work of Gomberg, who has reserved this field, it is in itself quite distinct. We discovered that an oxygen compound was formed as the result of the action of sodium on a mixture of triphenylchlormethane and brombenzene, and the work which is now in progress was planned in order to find an explanation of the formation of this substance. We propose to investigate the action of sodium on ethereal solutions of triphenylchlormethane of varying concentrations. Experiments with a number of alkyl halides have shown that the concentration of the ethereal solutions of the halides is an important factor in the Wurtz synthesis. Preliminary experiments seem to indicate that with triphenylchlormethane the concentration determines whether a reaction takes place or not.

The action of sodium on a mixture of carbon tetrachloride and brombenzene is also being studied. This reaction it is hoped will yield tetraphenylmethane. The fact that Polis[1] obtained an almost theoretical yield of silicon tetraphenyl by an analogous reaction in which silicon tetrachloride was used, makes the study of carbon tetrachloride under the same conditions of especial interest. We have found in the case of carbon tetrachloride, that a reaction takes place readily in benzene or ethereal solution. When ether is the solvent, the reaction-product separates in large quantities. The results of these experiments will be published later.

As the method of carrying out the Friedel and Crafts reaction which we have employed, has given such a good result with carbon tetrachloride, other halogen compounds will be studied in the same way. It seems probable that the reaction-products may be obtained more readily, and that better yields may result. On account of the fact that the preparation of triphenylmethane by this reaction from chloroform results in the formation of a number of side-products, from which the hydrocarbon is obtained in pure condition with difficulty, this reaction will be first investigated.

EXPERIMENTAL.

The following directions for the preparation of triphenylchlormethane were found to give excellent results. Twenty-five grams of carbon tetrachloride and 50 grams of benzene are dissolved in 100 cc. of carbon disulphide. The flask containing the mixture is placed in ice-water and after about five minutes 30 grams of aluminium chloride are added. The evolution of hydrogen chloride begins in a few minutes and continues for one and a half to two days. At the end of this time the mixture is poured upon ice and vigorously stirred. The carbon disulphide is separated from the mixture, which is extracted twice more with carbon disulphide. The combined extracts are united, filtered, and evaporated almost to dryness, care being taken to avoid the presence of moisture. The crystals of triphenylchlormethane which separate, are treated with the smallest quantity of petroleum ether which will dissolve them. When the solution cools, the compound is obtained in the form of stout, radiating needles, at times one-half inch in length, which have a slight pink color. The product of this first crystallization usually melts at 100° to 102°. In order to obtain the compound in a high state of purity, it was dissolved in petroleum ether containing a small amount of carbon disulphide and boiled with dry bone-black. In this way colorless crystals were obtained. The melting-point was raised by this second crystallization to 105°–106°. When recrystallized a second time in the same way the compound melted at 108°–111°. Recrystallization did not change the melting-point. When great care was taken to get all of the triphenylchlormethane formed in the reaction a yield of 97 per cent was the result. Other experiments gave without special effort 79 and 83 per cent.

---

[1] Ber. d. chem. Ges., **18**, 1541; **19**, 1013.

Triphenylchlormethane dissolves readily in carbon disulphide, benzene, carbon tetrachloride, chloroform, and ether. It is much less soluble in petroleum ether. The substance is readily decomposed by water, and is slowly converted into triphenylcarbinol by the moisture in the air.

When a mixture of carbon disulphide, carbon tetrachloride, aluminium chloride, and benzene, in the proportions given above, was allowed to stand about three days, crystals appeared in the dark-brown oil, which was the product of the reaction. This oil eventually changed into a mass of crystals, which were purified by recrystallization. A quantity of the impure substance was dissolved in nitrobenzene. To separate portions of this solution, carbon disulphide was added in varying quantities. The resulting mixtures were put aside in flasks, which were corked to prevent evaporation. After four days the solutions were examined, and in the flask which contained 2 parts of nitrobenzene and 3 parts of carbon disulphide, large, well-formed, dark-brown crystals were found. These crystals decomposed rapidly in the air. Hydrogen chloride was given off and a coating of aluminium hydroxide was formed. The compound began to decompose at 122° to 125°. In order to obtain the crystals in pure condition for analysis, they were removed, one by one, from the mixture from which they had been crystallized, and were quickly covered with nitrobenzene. They were then placed in successive mixtures of nitrobenzene and carbon disulphide, which contained less and less of the nitro compound. The crystals were finally washed with pure carbon disulphide and quickly dried between filter-paper. The aluminium was determined by heating with concentrated nitric acid a weighed sample of the substance and finally igniting. The chlorine was determined by the Carius method (Analysis II), and by heating the compound with water, filtering, and estimating the chlorine in the filtrate (Analysis III).

The results of the analyses follow :

I. 0.2918 gram substance gave 0.0368 gram Al_2O_3.
II. 0.3224 gram substance gave 0.4457 gram AgCl.
III. 0.2874 gram substance gave 0.3996 gram AgCl.

	Calculated for $Al_2Cl_6.2(C_6H_5)_3C.Cl$.	Found.		
		I.	II.	III.
Al	6.60	6.68	....	....
Cl	34.63	....	34.43	34.40

The compound was heated with water and the triphenylcarbinol was filtered off and weighed. The amount obtained was 57.98 per cent instead of 63.02 per cent, the amount required by theory. This low result was shown to be due to the fact that the carbinol was volatile to some extent with the water that was driven off in drying it. Some crystals which were removed from the original reaction mixture before it had solidified, were analyzed without recrystallization, and were found to be quite pure.

BOSTON, MASS., November 12, 1900.

THE CONDUCTIVITIES OF SOME DOUBLE SALTS AS COMPARED WITH THE CONDUCTIVITIES OF MIXTURES OF THEIR CONSTITUENTS.

BY CHARLES F. LINDSAY.

Earlier investigations[1] in this laboratory have shown that the conductivities of solutions of double salts differ greatly from the sum of the conductivities of the constituents. These differences are, in some cases, very large indeed, in the more concentrated solutions, and gradually become less and less as the dilution increases. The fact that the sum of the conductivities of the constituents is greater than the conductivity of the double salt, indicates that the double salt does not dissociate in solution in the same way as its constituents; *i. e.*, it does not break down into its constituents and then each of these dissociate as it would if alone in the solution.

---

[1] Jones and Mackay : This JOURNAL, **19**, 83; Jones and Ota : *Ibid.*, **22**, 5; Jones and Knight : *Ibid.*, **22**, 110.

The conclusion which has been reached is that double salts in concentrated solution dissociate to a greater or less extent as if they were salts of complex acids, and, then, as the dilution increases, the complex ion dissociates into the simplest ions. Since the differences found with the double chlorides, bromides and iodides are larger than with the double sulphates, an example will be taken from one of these classes to make the above point clear. Take the double bromide of barium and cadmium, $BaBr_2CdBr_2$. The conductivity of the double salt[1] at a volume of two is about thirty per cent less than the sum of the conductivities of the constituent bromides at this dilution. This difference rapidly diminishes with increase in dilution until at 100 liters it is about 8 per cent, and at 1,000 liters about 4 per cent. These results can be explained best by assuming that in the more concentrated solutions some of the double molecules are electrolytically dissociated thus:

$$BaBr_2CdBr_2 = \overset{++}{Ba} + \overset{=}{CdBr_4},$$

While, with increase in dilution, the complex ion, $\overset{=}{CdBr_4}$, breaks down more and more into the simple ions,

$$\overset{++}{Cd} + \overset{-}{Br} + \overset{-}{Br} + \overset{-}{Br} + \overset{-}{Br}.$$

At a dilution of 10,000 liters the salt is almost completely dissociated into its simplest ions.

The differences between the conductivity of the double salt and the sum of the conductivities of its constituents are considerably smaller for the double sulphates than for the double halides, but even with the double sulphates the differences are too large to be accounted for on the ground that each constituent would drive back the dissociation of the other. That this influence would come into play in all solutions which are not isohydric is well known, but it was shown that this would not account even for the cases where the smallest differences were found.

---

[1] This JOURNAL, **22**, 132.

In connection with the above work some measurements had been made which indicated that the conductivity of a double salt is not exactly the same as the conductivity of a mixture of its constituents, having the same concentration as the double salt. This result, if true, would be so surprising that it seemed very desirable to investigate the question as thoroughly and carefully as possible. The work described in this paper was undertaken, then, to determine whether there is any difference between the conductivity of a double salt and the conductivity of a mixture of the constituents of the double salt having the same concentration. This investigation was extended to two double sulphates and one double chloride.

General Method of Work.

The double salt was prepared by weighing out the constituents as nearly as possible in the proportion in which they occur in the double salt in question, dissolving these and evaporating to crystallization. The double salt, which was always obtained in well-defined crystals, was dried by filter-paper, and when enough had been obtained for work the whole preparation was fairly sampled and carefully analyzed. In this way the purity of the double salt was established. A solution of the double salt was prepared having approximately the concentration desired, and the solution standardized by analysis. The more dilute solutions were prepared by suitably diluting this mother-solution in measuring flasks. In a number of cases the more dilute solutions were analyzed directly to avoid any possibility of error in making the dilutions. All the water used was prepared by the method of Jones and Mackay.[1] The preparation of solutions containing the mixture of the constituents of the double salt was more difficult. In most cases the following method was adopted: A solution of approximately the desired concentration of each of the constituent salts, which had been very carefully purified, was prepared. Each solution was then standardized gravimetrically. These standardizations were repeated in every case until it was certain that the result was correct to 0.1 of one per cent. From these analyses the volumes of the two solutions which would contain the constituent salts in the same proportion in which they occurred in the double salt, were calculated. These volumes of the two solutions were mixed in a measuring flask and the whole diluted to a known volume. This solution, containing a mixture of the constituents of the double salt was then standardized gravimetrically, to see that no error had beed made in bringing the constituents together and in diluting them to a known volume. This standardized solution, which in every case was found to contain the constituent salts to almost exactly the extent which we had calculated, was used as the mother-solution. The more dilute solutions of this mixture were prepared from this mother-solution by diluting measured volumes in a measuring flask. In these cases, also, a number of the more dilute solutions were standardized directly.

---

[1] This JOURNAL, 19, 91.

In one or two cases the mother-solution of the mixtures was also prepared by bringing together weighed quantities of the dried salts, dissolving the mixture, and diluting to a known volume. In such cases the solution was also standardized gravimetrically. This method of preparing solutions of mixtures was simply used as a check on the method first described.

By preparing the solutions as above described I was confident that I knew the concentration of the double salt to 0.1 of one per cent, and I was equally confident that I had mixed the two salts in the same proportion in which they occur in the double salt, and had standardized the solution of the mixture to within about the same limit of error.

The same cell was used to measure the conductivity of the double salt as was used with the mixture. Some of the same water was used in making the solutions of the double salt and of the mixture of the constituents. Similarly, the same thermostat, thermometer, Wheatstone bridge, and resistance box were always used in both cases. The cell was frequently restandardized, and temperatures (25°) were accurate to 0°.1. The conductivities of the solutions of double salt and of mixture were thus measured under as nearly the same conditions as possible. It now remains to be seen what results were obtained.

Double Chloride of Potassium and Cadmium,
$KCl.CdCl_2$.

The volumes are tabulated under v, the molecular conductivities under μ_v. All measurements were made at 25°.

	Double salt, $KClCdCl_2$.	Mixture of $KCl + CdCl_2$.	
v.	μ_v.	μ_v.	Difference.
2	117.8	119.4	1.6
4	146.3	148.1	1.8
8	172.4	174.9	2.5
20	208.4	209.3	0.9

The conductivity of the double chloride is, thus, less than the conductivity of the mixture of the two chlorides. The difference in this case is always small, but is larger than any known experimental error, and is always on the same side; *i. e.*, the mixture at all of the dilutions studied, has the higher conductivity. The difference here is, however, so small that if this was the only case studied it would arouse no special interest. Other cases have, however, been studied.

Double Sulphate of Potassium and Nickel,
$K_2SO_4.NiSO_4$.

The volumes at which the conductivities of the double salt and the mixture were measured are slightly different in this case. The values actually found were:

	Double salt, $K_2SO_4.NiSO_4$.		Mixture of $K_2SO_4 + NiSO_4$.
v.	μ_v.	v.	μ_v.
5.836	212.80	6	216.31
11.672	243.08	12	246.61
23.344	271.46	24	276.02
58.36	313.38	60	314.35
116.7	346.00		

The following comparison is made at the volumes of the mixture, and the conductivities of the double salt at these volumes obtained by interpolation.

	Double salt, $K_2SO_4.NiSO_4$.	Mixture of $K_2SO_4 + NiSO_4$.	
v.	μ_v.	μ_v.	Difference.
6	213.68	216.31	2.63
12	244.38	246.61	2.23
24	273.31	276.02	2.71
60	314.13	314.35	0.22

The difference here is somewhat larger than in the case of the double chloride, and is again always on the same side; *i. e.*, the conductivity of the double salt is always smaller than that of the mixture at the same concentration. The difference here tends to grow less with increase in dilution, and it looks as if it might entirely disappear at greater dilutions.

Double Sulphate of Ammonium and Magnesium, $(NH_4)_2SO_4.MgSO_4$.

The volumes at which the conductivities of the double salt were measured were different from those for the mixture. The following results were obtained:

	Double salt, $(NH_4)_2SO_4.MgSO_4$.		Mixture of $(NH_4)_2SO_4 + MgSO_4$.
v.	μ_v.	v.	μ_v.
1.608	149.7	2	164.6
3.216	189.8	4	202.4
6.432	224.8	8	237.1
16.08	265.6	20	277.9
32.16	298.6		

Interpolating the conductivities of the double salt for the volumes at which the mixture was studied, we have:

	Double salt, $(NH_4)_2SO_4.MgSO_4$.	Mixture of $(NH_4)_2SO_4 + MgSO_4$.	
v.	μ_v.	μ_v.	Difference.
2	159.7	164.6	4.9
4	197.7	202.4	4.7
8	231.5	237.1	5.5
20	273.9	277.9	4.0

The differences here are larger than in either of the other cases investigated, and again show that the double salt has a smaller conductivity than the mixtures of its constituents.

The differences in this case remain practically constant with change in dilution, but the greatest dilution used is not very high, and it might be that the difference would disappear in this case also with higher dilutions.

From these results we are led to the conclusion that the conductivity of a double salt in concentrated solutions is slightly less than the conductivity of a mixture of the constituents having the same concentration as the double salt. It looks as if the double salt, when once formed, did not dissociate in exactly the same way or to the same extent as the mixture of the constituents which had never united to form the double salt. This conclusion was so different from what we should expect that it was decided to test it in another way. The conductivity of a solution of the mixed salts was determined and a measured volume of the mixture then placed in a platinum dish and evaporated to dryness. Under these conditions there would be at least some of the double salt formed. This residue was then dissolved in some of the same pure water in which the mixture of the two salts was originally dissolved, and diluted to exactly the same volume. If the double salt has a smaller conductivity than the mixture of the constituents at the same dilution, the second solution containing the residue from the evaporation should have a smaller conductivity than the original solution of the mixtures at the same concentration.

The experiment was tried with the double sulphate of potassium and nickel. A solution containing the two sulphates in equimolecular quantities was evaporated nearly to dryness in a platinum dish, the residue dissolved and diluted to exactly the original volume. The volume of the solution was 24 liters. The following results were found :

$$K_2SO_4 + NiSO_4.$$

v.		
24	μ_v of mixture before evaporation	276.02
"	" " " after "	274.59
"	" " double salt	273.31

In a second experiment a more concentrated solution was employed, where $v = 12$.

v.

12 μ_v of mixture before evaporation	246.61
" " " " after "	245.14
" " " double salt	244.38

In both of these experiments the mixture before evaporation had a larger conductivity than after evaporation. This agrees exactly with what was found above, since in the process of evaporation some of the double salt was formed by a union of the constituents. It will be observed that the mixture, after evaporation, had a larger conductivity than the solution of the double salt of the same concentration. This is also what is to be expected since, in the rapid evaporation, only some of the double salt was formed. Indeed, it could be readily observed with the eye that the residue, after evaporation, was a mixture of the double salt and the constituent sulphates.

These experiments confirm, then, the results of the direct measurement of the conductivities of double salts and of mixtures of their constituents. In concentrated solutions, at least, the mixtures have the higher conductivity.

In conclusion, I wish to express my thanks to Dr. H. C. Jones, at whose suggestion this investigation was undertaken and carried out.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY.

Contributions from the Chemical Laboratory of Lehigh University.

V.—THE ACTION OF SULPHURIC ACID ON PHENETOL.[1]

BY WILLIAM B. SCHOBER AND HENRY L. BOWERS.

The published statements of the different observers who have studied the action of sulphuric acid on phenetol (ethylphenyl ether) are not in accord, probably because the experimental conditions were not the same. Opl and Lippmann[2] heated pure phenetol, boiling at 168° to 170°, with an equal weight of English sulphuric acid on a water-bath for an hour and a half. They obtained two isomeric sulphonic acids, named by them phenetolsulphonic acid and phenetolparasulphonic acid, and found that the barium salt of the former was difficultly soluble in hot water, while that of the latter dissolved easily in cold water.

---

[1] From the thesis of Henry L. Bowers, submitted to the Faculty of Lehigh University for the degree of Analytical Chemist, June, 1900.

[2] Ztschr. Chem, 1869, 470.

Moody[1] finds that, contrary to the statements of Kekulé, and Opl and Lippmann, anisol and phenetol, when treated with sulphuric acid, yield *only* the parasulphonic acid. He says: "phenetol like anisol on sulphonation either with sulphuric acid or chlorsulphuric acid, either warm or in the cold, gave rise only to the para acid." Lagai[2] controverted Moody's statement and asserted that he had isolated a second acid from the product obtained on sulphonating phenetol; he described its amide as crystallizing from water in feathery needles melting at 142°, but he gave no analyses or other evidence to show that it was a derivative of phenetol. Moody, by an indirect method, prepared the amide of orthophenetolsulphonic acid. It forms long flexible needles, melting at 156°.

One of us, several years ago, studied the action of sulphuric acid on anisol (methylphenyl ether)[3] under different conditions, and found that anisoldisulphonic acid was formed in every case in which the reacting substances were heated to 92°, the quantity increasing with an increase in the proportion of sulphuric acid and increase in time of heating.

Paranisolsulphonic acid was formed in every case, the amount decreasing with increase of temperature, time of heating, and excess of sulphuric acid.

Orthoanisolsulphonic acid was formed in small quantities when anisol and sulphuric acid were allowed to react at ordinary temperatures. It was not formed when the proportion (by weight) of sulphuric acid to anisol was greater than 4 : 1.

This investigation was undertaken for the purpose of studying the reaction between sulphuric acid and phenetol under varying conditions. The conditions of the experiments described below were so arranged that the results could be com pared with those obtained in studying the action of sulphuric acid on anisol. In this way the difference or similarity in behavior of the two ethers toward sulphuric acid will be shown.

---

[1] Proc. Chem. Soc., 1892, p. 90, 214.

[2] Ber. d. chem. Ges., **23**, 3392.

[3] This JOURNAL, **18**, 858.

Other investigations are in progress in this laboratory having for their object the study of the action of sulphuric acid toward the higher members of that class of mixed ethers of which anisol and phenetol are the first two.

Experiment I.

In this and the other experiments, the phenetol used was Kahlbaum's preparation, a clear, colorless liquid boiling constantly at 172°; the sulphuric acid was "concentrated chemically pure."

Fifteen and two-tenths grams of phenetol and 15 grams of sulphuric acid were mixed and allowed to stand at the room temperature (21°) for three hours. When the acid was poured into the ether the liquid became faintly red and a slight evolution of heat was noticed. The reaction-mixture was cooled from time to time in order to prevent the temperature from rising above 21°. Upon pouring it into a large quantity of water, 5 cc. of phenetol separated out. This was removed, and the acid solution neutralized with barium carbonate. The barium sulphate was filtered off and washed repeatedly with hot water. The barium salt was converted into the sodium salt by precipitation with sodium carbonate, the barium carbonate thus formed was filtered off, and this was also repeatedly washed with hot water. The solution of the sodium salt was evaporated to dryness on a water-bath, and then heated to 110° in an air-bath. The dried product weighed 14 grams. This was ground to a fine powder and treated with phosphorus pentachloride. The action was so energetic that it became necessary to cool the vessel and to add the halide in successive small quantities. The resulting sulphonchloride was poured into water and washed several times; it possessed a pinkish color and remained liquid in presence of water at 21°. After being purified, a concentrated solution of ammonia was poured over it and the mixture allowed to stand. The conversion into the amide took place slowly. The reaction-product was evaporated to dryness on a water-bath. In order to obtain the amide free from ammonium chloride, the mass was extracted with absolute alcohol. The alcohol was then evaporated off, the residue dissolved in hot water, and allowed to crystallize. Two substances were found ; they were separated by fractional crystallization. The one melting at 149° was assumed to be paraethoxybenzenesulphonamide,[1] the other melting at 128°, the meta compound.

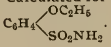
An analysis of the former gave the following results :

I. 0.2537 gram substance gave 0.4466 gram CO_2 and 0.1352 gram H_2O.

II. 0.3397 gram substance gave 0.3998 gram $BaSO_4$ (Carius method).

III. 0.1267 gram substance gave 0.1467 gram $BaSO_4$ (Carius method).

IV. 1.0206 grams substance gave 0.070447 gram N (Kjeldahl-Gunning method).

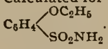
	Calculated for  $C_6H_4\begin{matrix}OC_2H_5\\SO_2NH_2\end{matrix}$.	Found.	
		I.	II.
C	47.73	48.01	....
H	5.48	5.92	....
S	15.94	16.18	15.90
N	6.99	6.92	....

The second amide found melted at 128°. Delisle and Lagai,[2] and Franklin[3] give the melting-point of the metamide as 131°. In a previous investigation the melting-point of the metamide was found to be 126°.

A partial analysis of the amide gave the following results :

I. 0.2030 gram substance gave 0.0013905 gram N.

II. 0.2118 gram substance gave 0.2484 gram $BaSO_4$.

	Calculated for  $C_6H_4\begin{matrix}OC_2H_5\\SO_2NH_2\end{matrix}$.	Found.
N	6.99	6.85
S	15.94	16.11

Weight of paramide, 8.11 grams.

Weight of metamide, 0.9 gram.

---

[1] Lagai gives the melting-point of the para compound at 149°.

[2] Ber. d. chem. Ges., **23**, 3392.

[3] Dissertation, 1894.

Experiment II.

In this and the following experiments the method of procedure was the same as that given in Experiment I. 15.2 grams of phenetol and 15 grams of sulphuric acid were mixed and allowed to stand six hours; the temperature remained constant at 21°. When the reaction mixture was poured into water, 4 cc. of the ether separated out. Two amides were found.

Weight of the paramide, 7.84 grams.
Weight of the metamide, 0.60 gram.

Experiment III.

This was a repetition of the preceding experiment except that the reacting substances were allowed to stand nine hours at a temperature of 21°. On pouring the mixture into water, 4 cc. of the ether separated out. Two amides were found.

Weight of the paramide, 8.0 grams.
Weight of the metamide, 0.59 gram.

Experiment IV.

15.2 grams of phenetol and twice the weight of sulphuric acid—30 grams—were mixed and heated on a steam-bath for thirty minutes. The temperature of the mixture during the heating was 90°. Two amides were found.

Weight of the paramide, 11.40 grams.
Weight of the metamide, 0.52 gram.

Experiment V.

The same quantities of phenetol and sulphuric acid used in the preceding experiment were mixed and heated on a steam-bath for sixty minutes. Temperature of the mixture during heating, 90°. Two amides were found.

Weight of the paramide, 10.27 grams.
Weight of the metamide, 0.46 gram.

Experiment VI.

This is a repetition of the two preceding experiments. The conditions were the same except the length of time—ninety minutes. The dried sodium salt obtained was decidedly pink in color. In the other experiments it was white. Two amides were found.

Weight of the paramide, 9.07 grams.

Weight of the metamide, 0.65 gram.

Experiment VII.

15.2 grams of phenetol and 60 grams of sulphuric acid were mixed and heated on a steam-bath for thirty minutes at a temperature of 90°. The dried sodium salt was pink. Two amides were found.

Weight of the paramide, 11.30 grams.

Weight of the metamide, 1.45 grams.

Experiment VIII.

The same quantities of the ether and acid as in Experiment VII were treated in the same way, except that the time of heating was twice as long—sixty minutes. The reaction-mixture assumed a deep reddish-brown color. The dried sodium salt was of a deep pinkish color. The sulphonchloride was dark-brown and solid at 22°. The solution of ammonia acted upon it slowly. The water into which the reaction-product, resulting from the treatment of the sodium salt with phosphorus pentachloride, was poured, yielded, upon evaporation, a considerable quantity of phenol. Small quantities of a dark-colored, gummy substance appeared during the crystallization of the amides. We were unable to obtain it in a pure condition. Two amides were found.

Weight of paramide, 3.10 grams.

Weight of metamide, 0.12 gram.

Experiment IX.

This is a repetition of Experiment VII, except that the time of heating was three times as long—ninety minutes. The sulphonchlorides formed a dark-colored, gummy mass, solid at 22°, which was apparently partially decomposed when treated with water. As in the preceding experiment, phenol was obtained on evaporating the water into which the sulphonchloride mixture had been poured.

Weight of the paramide, 1.96 grams.

If any of the metamide was formed it was impossible to obtain it pure, due to the presence of a considerable quantity of the gummy substance.

Experiment X.

This experiment was made in order to learn the effect of heating for a short time equal weights of phenetol and sulphuric acid. 15.2 grams of the ether and 15 grams of the acid were mixed and heated on a steam-bath for thirty minutes at a temperature of 90°. Two amides were found.

Weight of the paramide, 16.45 grams.
Weight of the metamide, 0.80 gram.

Experiment XI.

The same quantities of the ether and acid as in Experiment X were heated at the same temperature for twice the length of time—sixty minutes.

Weight of the paramide, 15.62 grams.
Weight of the metamide, 0.70 gram.

Experiment XII.

This was a repetition of Experiment XI. The time of heating, however, was ninety minutes. Two amides were found.

Weight of the paramide, 14.56 grams.
Weight of the metamide, 0.55 gram.

Experiment XIII.

In order to obtain a quantity of phenetoldisulphonic acid, 90 cc. of phenetol and the same volume of fuming sulphuric acid were mixed and heated on a water-bath at a temperature of 85° for thirty minutes. A portion of the reaction-product was converted into the amides. Four substances were found—the paramide in large quantity, exceedingly small quantities of the disulphonamide melting at 233°, a substance melting sharply at 189°, a substance melting at 142°. The last is undoubtedly the same compound that Lagai thought to be the orthoamide. Moody and Franklin give the melting-point of the orthoamide as 156°.

It is worthy of note that under the same conditions as those just given anisol forms a disulphonic acid with ease.

Summary of Results.

Experiment No.	Weight of acid.	Weight of phenetol.	Time of heating. Hours.	Temperature.	Weight of paramide.	Weight of metamide.
I	15	15.2	3	21°	8.11	0.90
II	15	15.2	6	21°	7.84	0.60
III	15	15.2	9	21°	8.01	0.59
			Minutes.			
IV	30	15.2	30	90°	11.40	0.52
V	30	15.2	60	90°	10.27	0.46
VI	30	15.2	90	90°	9.07	0.65
VII	60	15.2	30	90°	11.30	1.45
VIII	60	15.2	60	90°	3.10	0.12
IX	60	15.2	90	90°	1.96	...
X	15	15.2	30	90°	16.45	0.80
XI	15	15.2	60	90°	15.62	0.70
XII	15	15.2	90	90°	14.56	0.55

Conclusions.

Paraphenetolsulphonic acid was formed in every case in which sulphuric acid and phenetol were mixed and allowed to stand at the ordinary temperature or heated, the amount decreasing with the length of time the two substances were allowed to react at a temperature of 90°. At the ordinary temperature, the length of time the substances were allowed to react seemed to exert no appreciable influence.

When the proportion of sulphuric acid to phenetol was greater than 1 : 1 the amount of the paraphenetolsulphonic acid decreased with the increase in length of time of heating the reacting mixture.

Metaphenetolsulphonic acid was formed in every experiment but one—No. IX, in which the proportion of sulphuric acid to the ether was 4 : 1, and the time of heating ninety minutes. The figures obtained are to be regarded as only fairly accurate, owing to the small quantities in which the meta acid was formed and the great difficulty of freeing the metamide from a gummy impurity.

Phenetoldisulphonic acid was obtained when equal volumes of phenetol and fuming sulphuric acid were mixed and heated for thirty minutes at 85°. The quantity was minute.

South Bethlehem, Pa.

NOTES.

The New Radio-active Substances.

Since the last note on polonium and radium appeared in this JOURNAL, considerable work has been done on radioactive substances in general.

Debierne[1] found in the residues of pitchblende a new radioactive substance, differing from polonium and radium, and closely allied, as he thought, to titanium in its chemical properties. More recent work,[2] however, has led him to believe that it does not resemble titanium in all its reactions. The most active specimen of this new substance which he obtained consisted largely of thorium, as was shown by its chemical reactions, as well as by its spectrum analysis, and yet it does not resemble thorium in all of its reactions. Debierne calls it actinium. The rays from actinium possess the same properties as those of radium. They cause barium platinocyanide to fluoresce, produce photographic impressions and effect the ionization of gases. He thinks that the radio-activity of thorium compounds is due to the presence of minute quantities of actinium, and that thorium itself is inactive. Debierne[3] has also succeeded in producing induced radio-activity by precipitating barium sulphate in the presence of actinium, but found that it differed from radiferous barium sulphate in that the former showed no radium lines in its spectrum, and further, the activity of the former decreases in time and is finally lost, while that of the latter increases to a certain point and then remains constant.

Stoutt,[4] Becquerel,[5] and others have been working on the effect of a magnetic field on the Becquerel rays. The Becquerel rays in general are deflected in a magnetic field, while the Roentgen rays are not, and further, Becquerel showed that the rays emitted by a specimen of polonium nitrate are not deflected in a magnetic field as are those emitted by radium. In the case of radium some of the rays are deviated while others are not.

Curie[6] has proved experimentally that the deviable rays of radium are due to material emissions from the source of activity. He found that the emissions from radium charge bodies which receive them negatively, while the radium itself is charged positively. The non-deviable rays of radium seem to be of a different kind from the deviable rays or they have lost their electric charges. It has been urged against the material emission theory that if it be correct the radium emitting the rays ought to lose in weight, but it would be practically impossible to measure the loss in weight of radium due to emissions, because it has been calculated that it would require a million years for a specimen of radium to lose one milligram in weight. Debierne[1] found that the rays from actinium, like those from radium, are partly deviated in a magnetic field, and are charged negatively.

---

[1] Compt. rend., **129**, 593.
[2] Chem. News, **81**, 169.
[3] Compt. rend., **131**, 333.
[4] Chem. News, **81**, 61.
[5] *Ibid*., **81**, 121.
[6] *Ibid*., **81**, 145.

Bary[2] has carried on investigations with the view of determining what metals show luminosity in their salts under the influence of Becquerel rays. He found that such metals are lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, and barium. Of other metals, only the phosphorescent salts of uranium showed fluorescence. The author concluded that the same class of bodies which give salts phosphorescent to light also give compounds which are luminous under the influence of Becquerel rays. He regards the permanent luminosity of radio-active barium as due to the influence of Becquerel rays on the barium salt. But since the chemical properties of radium and barium are so similar, it may be that pure radium salts are fluorescent in the same manner as other metals of this class.

Demarçay[3] has recently again examined the spectrum of radium. The material was furnished him by Mdme. Curie and consisted of nearly pure radium chloride. He was unable to find any lines which were not present in his first spectral analysis of a more impure radium chloride, although the lines particularly characteristic of radium were much more intense than they were when previously observed.

Mdme. Curie[4] has redetermined the atomic weight of radium, using a specimen of radium chloride, which, to judge from the appearance of its spectrum, was but little less pure than the specimen which was furnished Demarçay for his spectrum analysis. The atomic weight was determined by estimating the chlorine in the anhydrous chloride of radium. In two determinations the results were 174.1 and 173.6. Since the specimen of chloride contained some barium chloride, the atomic weight of pure radium is doubtless considerably higher.

Giesel[5] has succeeded in obtaining a small amount of Debierne's actinium. He treated a concentrated solution of uranium nitrate with a small amount of a soluble barium salt and sulphuric acid. The resulting precipitate of barium sulphate was strongly radio-active, while the uranium nitrate had lost most of its radio-activity. The active barium sulphate, after conversion into a soluble barium salt, was treated with ammonia, and a small quantity of a very active substance was precipitated, while the remaining barium salt had lost its activity entirely. Radium could not have been separated from barium by ammonia, but actinium could, so Giesel concluded that the final radio-active substance which he obtained was a derivative of actinium.

---

[1] Chem. News, **81**, 169.
[2] *Ibid.*, **81**, 157.
[3] *Ibid.*, **82**, 73; Compt. rend., **131**, 258.
[4] Chem. News, **82**, 98; Compt. rend., **131**, 382.
[5] Ber. d. chem. Ges., **33**, 1665.

He also endeavored to separate polonium from bismuth, but in this was unsuccessful, and thinks that the so-called polonium is only a radio-active form of bismuth. He found the 0.5 gram of polonium, obtained from 500 kilograms of uranium residues, to consist entirely of bismuth hydroxide, $Bi(OH)_3$, which is also strongly radio-active, as is the oxychloride, BiOCl.

Several attempts have been made to determine whether radio-active uranium compounds can be rendered inactive by a transference of their radio-activity to other substances.

Becquerel,[1] by repeatedly treating uranium salts with barium chloride and precipitating the barium as sulphate, was able materially to decrease the radio-activity of the uranium salts, but could not make it disappear altogether.

Crookes[2] has been more successful. Since radium resembles barium so closely, he examined a large number of barium minerals, with a view of finding some of them containing radium, but all that he examined were inactive. He then examined a number of rare minerals, and found only those radio-active which contained thorium and uranium. The different salts of uranium showed about the same radio-activity.

It was possible, starting with a uranium nitrate which was strongly radio-active, to obtain by repeated crystallizations a nitrate which is entirely inactive, even though modifications in the physical or chemical conditions of the salt did not affect its radio-activity. Crookes showed that, when uranium nitrate is treated with ether, the portion which is dissolved by the ether shows no radio-activity, while the insoluble portion is much more strongly radio-active than the original salt.

He showed further that the radio-active substance in uranium can be precipitated by ammonia. When a solution of uranium nitrate is treated with ammonia, all the radio-active substance is found in the precipitate. He designates this radio-active substance found in uranium and its salts as UrX, which differs from polonium in that it is not volatile, while polonium is; and further the rays from UrX will pass through aluminium, lead, and glass, and those from polonium will not. Again, polonium is precipitated by hydrogen sulphide and UrX is not. UrX and radium also differ in many chemical properties, and Crookes thinks they are different substances, although he could not photograph lines in the spectrum of his UrX, because it was too weak. It is possible that his UrX and Debierne's actinium are identical. He thinks that radioactive thorium compounds can also be separated into inactive thorium and an active substance.

---

[1] Compt. rend., **130**, 1583; **131**, 137.
[2] Chem. News, **81**, 253.

Quite recently, Hofmann and Strauss[1] have succeeded in isolating radio-active lead salts and radio-active rare earths from uranite, pitchblende, bröggerite, cleocite, samarskite, and euxenite. In the products which were obtained it was impossible to detect traces of uranium, thorium, polonium, radium, bismuth, barium, or titanium. It seems particularly interesting that radio-active substances should have been obtained from bröggerite, which was absolutely free from uranium and thorium. These authors have also confirmed the work of Crookes in obtaining entirely inactive uranium from a strongly radio-active specimen. C. E. C.

On the Nature of the Oxyazo-Compounds.

In my article "On the Nature of the Oxyazo-Compounds" printed in this JOURNAL (Vol. 22, 364), the statement is made that the free paraoxyazo compounds do not react with phenylhydrazine. I find, however, that when paraoxyazobenzene is heated to 100° with an excess of phenylhydrazine, a slow decomposition occurs attended by the evolution of nitrogen and the formation of a white, crystalline body. Other oxyazo compounds under the same conditions show a similar action. This reaction is now being studied in this laboratory.

OHIO STATE UNIVERSITY,
December 15.

WILLIAM MCPHERSON.

REVIEWS.

CHEMICAL TECHNOLOGY, or Chemistry in its Applications to Arts and Manufactures, edited by CHARLES EDWARD GROVES, F.R.S., and WILLIAM THORP, B.Sc.; VOL. III, GAS LIGHTING, by CHARLES HUNT, Manager of the Birmingham Corporation Gasworks. Philadelphia: P. Blakiston's Son & Co. 1900. pp. xviii + 312.

The first volume of this work was devoted to "Fuel and Its Applications," treated of by E. J. Mills and F. J. Rowan, and was published in 1889 in England and the United States.

---

[1] Ber. d. chem. Ges., 33, 3126.

The second volume, on "Lighting by Solid and Liquid Illuminants," by W. Y. Dent, J. McArthur, L. and F. A. Field, B. Redwood, and D. A. Louis, appeared in 1895. It was announced that the third volume would include the subjects of "Gas Lighting, Electric Lighting, Lighthouse Illuminations, and Photometry," but of these the first only appears in the volume now issued. In general plan and character it much resembles those that have preceded it. There is presented a large mass of valuable information, not very well ordered or marshalled, and rather unequal in regard to the fulness of detail of different parts of the subject. In a monograph aiming at completeness one might fairly expect to find, not merely numerous analyses of British gas coals, but like analyses of the materials in use in other countries. The production in France of illuminating gas from the "suint" of wool washing is not mentioned at all, nor is there any notice of rosin or wood gas; a few pages are given to the manufacture of "oil gas" from hydrocarbon shale oil (not the original oil gas of the early part of this century, from which Faraday first obtained benzene), but arrangements tried in the United States for making gas from petroleum are not noticed. Among the most valuable chapters are those on modern types of regenerative furnaces for heating coal-gas retorts, on machinery for charging the retorts and withdrawing the coke from them, and on gas burners, including regenerator and incandescent burners. In connection with the last named appliances one misses the interesting results of v. Welsbach's investigation of the character (color) of the light from mantles prepared with the various rare earths which he has brought into use. Acetylene from calcium carbide is inadequately treated; much of the knowledge in regard to it, and to the conditions for its safe employment, which has been acquired within the last few years should have been collated and discussed. A number of subordinate points in the book are quite interesting, for example, the question of the circumstances affecting the formation of naphthalene deposits in coal-gas mains. As a whole, the work should find a place in every general collection of technological literature. J. W. M.

L'EAU DANS L'INDUSTRIE, par H. DE LA COUX, ingénieur-chimiste expert près le Conseil de Préfectur de la Seine, etc. Paris: V^{ve.} Ch. Dunod. 1900. pp. 496.

Many of the modern technical works on water supply devote a chapter or so to the relations of water to special manufactures, but usually the space so used is small, and the subject is treated in a very condensed and general way. The book now noticed does not discuss the general use of natural waters for drinking and other domestic purposes, but is concerned altogether with industrial applications. It is a well-arranged and valuable manual—not absolutely exhaustive, but on the whole satisfactorily covering the field proposed. It contains an extensive, detailed, and well-illustrated discussion of boiler incrustation and boiler corrosion, both in relation to ordinary fresh waters and also to sea water and the waters from mines, the means of dealing with such troubles, different types of boiler, preheating arrangements, chemical treatment of the water, etc. The special considerations are gone over which affect the use of water for soap-making, washing on the industrial scale, flax steeping, wool cleansing, bleaching, dyeing, tanning, paper-making, photography, sugar refining, brewing, distilling, etc. Means and apparatus are described for the purification of water intended for various special purposes, including filters, filter presses, and other mechanical appliances. There is an extended discussion of the treatment of residual watery liquids from various sources, mixed sewage, soapy water, and the recovery from it of glycerol. The book closes with chapters on analytical methods, qualitative and quantitative. There are numerous and generally good illustrations accompanying the text. Like most French scientific books, it has a good table of contents at the end, but no index. J. W. M.

THE OIL CHEMIST'S HANDBOOK. By ERASTUS HOPKINS, A.M., B.SC., Chemist in charge of U. S. Laboratories, Boston, Mass. New York: John Wiley & Sons. 1900. pp. viii + 72.

This book is intended to present, in condensed form, the chief approved methods for testing fixed oils, fats and waxes for commercial purposes—hydrocarbon oils are only considered in their relations as adulterants. The descriptions of analytical processes are much too brief to guide safely anyone depending upon the book for instruction, and in some cases they are altogether inadequate, as, for example, in the few lines devoted to the quantitative determination of glycerol.

The tables in which the fats and oils are arranged, not alphabetically, but in the order determined by particular reactions, such as the saponification value, are convenient. More exact references to the authorities for individual results would have added to the usefulness of these tables. There are some statements of value in regard to special methods of adulteration.

The very brief discussion of points involving general chemical principles is marked by, to say the least, loose and unfortunate expression, and the language of the book as English is not above criticism. J. W. M.

GRUNDLINIEN DER ANORGANISCHEN CHEMIE. Von WILHELM OSTWALD. Mit 122 Textfiguren. Leipzig: Verlag von Wilhelm Engelmann. 1900. pp. 795. 8vo.

At last a serious attempt has been made to present the subject of inorganic chemistry in the light of the results which have been achieved in the field of physical chemistry. Probably no one is better fitted for this work than the writer of the book before us. Certainly no one has done more to make a place for physical chemistry than Ostwald, so that this book will attract an unusual amount of attention, and it deserves much more than a passing notice. The first feeling experienced by one who, though not a physical chemist, is much interested in the work in progress in that field, is that of relief to find that so much is left of the old structure. In his preface the author says he has retained as much as possible of the old forms: "Was ich beibehalten habe ist zunächst die naturhistorische Anordnung des Stoffes. Mann könnte vielleicht schon jetzt den Versuch wagen, die Chemie von vornherein als eine rationelle Wissenschaft auf Grund einiger Prinzipien aufzubauen, und die Beschreibung der verschiedenen Stoffe als Erläuterungen dieser allgemeinen Gesetze einzuführen. Was mich hiervon abgehalten hat, ist nächst dem Bedürfnisse des geschichtlichen Zusammenhanges die Erkenntniss gewesen, dass die Mannigfaltigkeit der verschiedenen Stoffe zu gross und ihre Einzelkenntniss zu wichtig ist, als dass eine solche Darstellung gegenwärtig für den Unterricht sich verwerthen liesse." However objectionable it may appear, it is still necessary, and it is likely to remain necessary, to study things as well as the laws that govern their action upon one another. The author clearly recognizes this, and consequently he deals to as great an extent with *things* as others do. The old things are still there, and the old laws. Some of the old conceptions have, to be sure, been pushed into the background, and the view will not appear familiar to the majority of chemists.

The author has practically abandoned the atomic theory, Avogadro's hypothesis, and the Periodic Law. They are all mentioned but so that the student will get the impression that they are of little value. Thus, on page 155, he says: "Die Aufstellung der Atomhypothese in dem hier entwickelten Sinne ist im Jahre 1805 durch J. Dalton erfolgt; die Prüfung ihrer wichtigsten Konsequenz, des Gesetzes der Verbindungsgewichte, ist von Berzelius ausgeführt worden. Durch die vollkommene Uebereinstimmung derselben mit der Erfahrung hat die Atomhypothese ein grosses Ansehen und eine allgemeine Anwendung erlangt, so dass sie noch gegenwärtig in der Chemie nahezu ausschliesslich herrscht.

"Auch in diesem Buche soll von diesem allgemeinen Gebrauch nicht wesentlich abgewichen werden. Doch läge es sicher im Interesse der Wissenschaft, wenn in dieser Beziehung eine grössere Vorsicht beobachtet würde, und deshalb ist hier Wert darauf gelegt worden, die Ausdrucksformen der Atomhypothese so sparsam anzuwenden, als es der heutige Sprachgebrauch nur gestattet."

The same caution is shown in presenting the molecular hypothesis commonly called "Avogadro's law," and in place of the conception of *molecular weight* that of *normal weight* is used. The normal weight of a gas is the weight of a volume of the gas as compared with the weight of the same volume of a hypothetical gas, the weight of which is 1/32 of that of the same volume of oxygen.

The periodic law is not referred to until the end of the book is reached, when nine pages are devoted to it. Its imperfections are emphasized and then follows this passage, p. 775: "Fragt man, wie man sich diesen und ähnlichen Unvollkommenheiten des periodischen Systems gegenüber zu stellen hat, so ist zu sagen, dass es sich hier nicht um ein Naturgesetz im strengen Sinne handelt. * * * Wir kennen, um ein Bild zu brauchen, von dem grossen Organismus der chemischen Thatsachen nur einen gewissen, zum Theil willkürlich geführten Querschnitt, während der übrige Körper uns fast ganz fremd geblieben ist. Es darf uns daher nicht wundern wenn wir die den ganzen Organismus beherrschenden Gesetze an diesem zufälligen Querschnitt noch nicht zu übersehen vermögen."

While it is undoubtedly true that all the facts of chemistry can be presented without the aid of the atomic hypothesis, the molecular hypothesis, or the periodic law, it cannot be denied that these are of great assistance in dealing with the facts. The conceptions "normal weight" and "combining weight" are not as clear as molecular weight and atomic weight, though they appear to be free from speculation. Though the time may come when we shall be able to abandon the older conceptions, it will not come until we have something better to substitute for them. It does not seem to the reviewer that the conceptions that Ostwald makes use of are better.

The only danger in the atomic hypothesis is that which attaches itself to every hypothesis. Many will overwork it. For the clear thinker this danger does not exist, and there is no method of dealing with facts that will prevent the average student from going astray.

As regards the periodic law, is it not true that inorganic chemistry has become much more interesting since this law, however imperfect it may be, has been recognized? And is it wise to throw away this advantage because of the imperfections of the law as we at present know it?

The chief interest in the book before us is connected with the introduction of the results of investigations in the field of physical chemistry. Ions pervade the book. Catalysis is often introduced to *explain* curious phenomena. The Law of Mass Action is presented by means of a few examples. The Phase Rule also comes in for its share of attention. There is no serious difficulty in presenting the conception of ions and showing the connection between this conception and facts that are constantly dealt with in the laboratory. There is, however, the same danger here that is presented by the atomic hypothesis. Ions can easily be overdone. It will hardly be claimed that the ion is entirely free from speculation. There is difficulty in making the Phase Rule and the Law of Mass Action clear in the early stages of the study of chemisty for the reason that the reactions that illustrate them best are not every-day reactions, and therefore, even after learning what the laws are, the student fails to see the connection between them and the phenomena he commonly has to deal with. No doubt the connection exists, but in most cases it cannot be recognized.

A careful examination of this book has not destroyed the impression that the incorporation of the conceptions of physical chemistry into a course in general inorganic chemistry involves grave difficulties. However heterogeneous the facts of inorganic chemistry may appear, we cannot disregard them. They must be mastered. Ostwald concedes this. Physical chemistry as such cannot take the place of what some call old-fashioned chemistry, but undoubtedly old-fashioned chemistry can be improved by physical chemistry, and all chemists owe a debt of thanks to Ostwald for his effort to show how this improvement can be brought about. Every chemist should own a copy of this book, and should conscientiously study it.

I. R.

ACETYLENE, A HANDBOOK FOR THE STUDENT AND MANUFACTURER. By VIVIAN B. LEWES F.I.C., Etc., Professor of Chemistry, Royal Naval College, Greenwich, Chief Superintending Gas Examiner to the Corporation of the City of London, etc., etc. With 228 illustrations. Macmillan Co. 1900. pp. 978.

The publication of this book fills a gap in chemical and technical literature, for despite the importance of the subject no handbook of acetylene existed in the English language, nor were the German and French text-books sufficiently comprehensive to satisfy the chemist, as all of them were written by engineers presenting the subject from the technical point of view. Professor Lewes is a chemist, a noted expert in the chemistry and technology of artificial light, and has since the first introduction of acetylene done much work on its use as an illuminant. Indeed, the searcher for knowledge of acetylene has hitherto found the scattered articles of Lewes his most reliable source.

A handbook of acetylene must be available for the chemist, the technologist, the manufacturer, and the inventor. To this end the author divides his book into three parts.

Part I, *Scientific* (169 pages), gives in four chapters the history of acetylene, its preparation, its properties, its chemical reactions. Everything of importance bearing on the subject, even work of little apparent importance, will be found here. The treatment is clear and well-proportioned, and references to the original articles are everywhere given. The space given to the brilliant work of Berthelot, Vielle, Moissan, Haber and Oechelhausen, Gerdes, and others is ample, and the more important experiments and conclusions are given in the form of extracts from the original articles.

The following extract from Lewes's own work may be of interest: "Experiments made by withdrawing the gases from various parts of luminous flames show that no matter what is the initial character of the hydrocarbon present, acetylene is always produced before luminosity makes its appearance, and moreover that the illuminating power of the flame follows the ratio of acetylene so produced; and this fact, taken in conjunction with the observation that when acetylene free from air is allowed to flow through a Jena-glass tube heated up to a temperature of 780° C., it is decomposed with luminosity, whilst the carbon set free in flowing forward through the zone of heat is perfectly non-luminous, formed the basis of what is now known as the acetylene theory of luminosity.

"Stated in its simplest form, this theory is as follows: In the same way in which the decomposition of the acetylene in flowing through a heated tube endows the carbon particles with a luminosity which the heat of the tube alone is unable to impart, so does the decomposition of the acetylene generated in a hydrocarbon flame increase the light-yielding power of the carbon particles liberated by its decomposition over what might have been the light emitted had they only been heated to the temperature of the flame itself. * * * * Lewes gives the temperature of decomposition of acetylene as 780° C., whilst Haber places it between 770° and 790° C. Frank, however, gives it as above 1000°, though upon what evidence is not clear." This subject, in its practical bearings, is discussed historically and fully in a later chapter.

Part II, *Technical* (489 pages), describes in seven chapters the electric furnace and its application to calcium carbide (33 electric furnaces are described); the manufacture, properties, and impurities of calcium carbide; the generation of acetylene; the impurities of commercial acetylene; and the processes adapted for their removal; the generation of light and power from acetylene; the utilization of diluted acetylene; the analysis of material for carbide manufacture; and of carbide and acetylene.

Those who have paid little attention to the acetylene industry will be surprised at the bewildering number of furnaces, methods, generators, lamps, and burners offered to the public. Only a skilled technologist can find his way through this maize. The author groups the furnaces, generators, etc., into types, shows by experiment the relative advantages of each type, and points out wherein the individual inventions are better or worse than their type average.

The chapter on the utilization of diluted acetylene is of particular interest, especially as more than half of the acetylene made abroad is not burned pure, but is used for enriching Pintsch gas for car illumination on the German railways, and has been recently introduced on the English railways. It will be remembered that the attempt was made in this country a few years ago to enrich water-gas with acetylene, and that the attempt failed; it was found that nearly 24 per cent of acetylene is required to enrich non-luminous water-gas to the average illuminating value, the mixture of hydrogen and carbon monoxide having the effect of practically destroying the illuminating power of acetylene. At the same time it was found that additions of acetylene to poor *carburetted* water-gas developed the theoretical enrichment value of the former. In investigating this and some similar phenomena, Lewes's experiments proved that of the so-called diluents, methane is the only one capable of developing the great illuminating or enrichment value of acetylene, and that it is to the presence of methane in poor coal-gas and in poor carburetted water-gas that the enrichment caused by small additions of acetylene is due.

This led Lewes to devise an ingenious method for charging water-gas with methane at slight cost, the product enriched with small percentages of acetylene being an illuminating gas of good average candle power.

Part III includes the legal enactments in force in various countries with regard to the use of acetylene, and a list of English patents of generators and burners with brief descriptions of each. The patent list occupies 147 pages with an average of five patents to a page, making over 700 patents.

In conclusion it may be noted that while the reader marks with regret the utilization of so many of the beautiful waterfalls of Europe for generating electric power, bringing as it does the desecration of the most hidden and beautiful nooks by factory and workman's village, still the movement of branches of industry dependent on electric current or employing cheap power from the seaboard and plain to sparsely populated mountain districts is of interest and indeed of the greatest importance in the distribution of wealth and population. This movement has been developed chiefly hitherto by the carbide industry; thus Spain and Norway are absorbing capital which is to change lone mountain regions into manufacturing centers.

The publishers should be congratulated on this well printed and lavishly illustrated volume. E. R.

Commercial Organic Analysis. By Alfred H. Allen, F.I.C., F.C.S. Volume III, Part 1; Tannins, Dyes, and Coloring Matters, Writing Inks. Third edition, revised and enlarged, by J. Merritt Matthews, Ph.D., Professor of Chemistry and Dyeing in the Philadelphia Textile School. Philadelphia: P. Blakiston's Son & Co. 1900. pp. xvi + 589. Price $4.50.

The revision of this volume has greatly increased its usefulness. The section on tannins is enlarged by the description of some new tannin materials and several new methods of analysis. The chapter on Dyes and Coloring Matters has undergone considerable change, as might be expected, considering the great number of dyes that have come into use since the second edition of this work was printed. The dyes have been reclassified in a better way, the chapter rewritten in part, and descriptions of a great many new dyestuffs included in the tables. The analytical tables have also been amplified, and new tables added. Many new dyes are described in the text, but more could very well have been added, with elimination of some dyes now unimportant, which are retained from the older volume.

Minor defects are present, as might be expected. The footnotes often run over to another page; many of them could have been incorporated in the text, with greater comfort to the reader. The method of rendering substantive cotton colors faster to washing and light by diazotizing and developing with phenols or amines does not receive the notice that its importance deserves. The second formula for tartrazin on page 139 has two SO_3Na groups missing. The formula $C_6H_5.N{:}N.Cl$ and the name diazobenzene chloride (page 142) is retained, instead of $C_6H_5.\underset{\overset{\vdots}{N}}{N}.Cl$, diazonium chloride. Other cases might be cited where the revision has not been carried far enough.

This edition is in general "up-to-date," and those who deal with dyes will find it advantageous to put it in the place of the corresponding volume of the second edition of this work. G. S. F.

VOL. XXV. FEBRUARY, 1901. NO. 2.

AMERICAN

CHEMICAL JOURNAL

ON THE BEHAVIOR OF IODINE AND BROMINE TOWARDS CHLORINE HEPTOXIDE AND PERCHLORIC ACID.

BY ARTHUR MICHAEL AND WALLACE T. CONN.

The first results indicating the property of iodine to replace chlorine in its oxygen acids, which is at present generally accepted as a fact, may be found in the investigation of Humphry Davy[1] on iodine, who discovered iodic acid by treating the element with chlorine monoxide, hypochlorous acid, or chlorine dioxide. Millon[2] subsequently found that iodine heated with aqueous potassium chlorate and a small quantity of nitric acid yields potassium iodate. In 1835 Balard[3] noticed that hypochlorous acid reacts with bromine to form bromic acid, but, contrary to his expectation, as the "electronegative tendency of bromine is much less than that of chlorine," he was unable to realize this synthesis by using chlorine dioxide, or a concentrated solution of chloric acid.

These reactions were considered to be oxidations, and the conception of a direct replacement of chlorine by iodine or bromine is based on the observations of H. Kaemmerer. According to this work the following reactions may be realized :

---

[1] J. Phys. **77**, 456.

[2] Ann. chim. phys. [3], **9**, 400.

[3] J. prakt. Chem., **4**, 169.

I. Hot aqueous chloric acid and bromine give traces of bromic acid, which, however, is difficult to detect, as it is usually destroyed.[1]

II. Bromine reacts easily with the vapor of hydrated perchloric acid to form perbromic acid.[2]

III. A concentrated solution of perchloric acid heated with iodine gives periodic acid and chlorine.[3]

Evidence soon accumulated which went to show that some of the statements made by Kaemmerer in these researches are not trustworthy. J. Thomsen[4] proved that the heat of formation of aqueous bromic acid is considerably less than that of aqueous chloric acid, which fact made the formation of bromic acid from bromine and chloric acid difficult to understand, and, as a much more competent investigator than Kaemmerer, Balard, had previously examined this question and found that no reaction takes place, it may fairly be assumed that this synthesis of bromic acid has never been realized. Then MacIvor,[5] Muir,[6] and Wolfram[7] endeavored to obtain perbromic acid from perchloric acid and bromine, but without success. Indeed, the last chemist showed that the liquid obtained by repeating the work of Kaemmerer really gave the reactions stated as characteristic for perbromic acid, but it consisted of perchloric acid, mixed with some sulphuric acid, which Kaemmerer used in this experiment to generate the perchloric acid. As Kaemmerer published no quantitative work on the subject, and based the existence of perbromic acid solely on these qualitative tests, it is obvious that perbromic acid never has had a serious claim for existence. That it cannot be formed from perchloric acid, we have shown still more conclusively, inasmuch as we find that pure perchloric acid is without action on bromine, even by long exposure to sunlight, or on warming; nor does chlorine heptoxide react with the element. The direct replacement of chlorine in chloric and perchloric acids by iodine from a thermochemical point of view is more probable than by bromine, since Thomsen[1] showed that the heat of formation of the oxy-acids of iodine is considerably greater than that of the corresponding chlorine acids. The formation of iodic acid from iodine and chloric acid, or any of the less oxidized oxy-acids, is therefore simply a question of oxidation. It is, however, the formation of periodic acid from perchloric acid and iodine, which has been considered a complete proof of the capability of iodine to replace chlorine, as the direct oxidation of iodine has never led to a higher state of oxidation than iodic acid, although hypochlorous and chloric acids have been used, which are much stronger oxidizers than perchloric acid. We have repeated this work of Kaemmerer, using pure perchloric acid of different concentrations, and find that there is not even a trace of periodic acid formed in this reaction, which proceeds by the oxidation of iodine to iodic acid. An analogous result was obtained from chlorine heptoxide, which leads to the formation not of iodine heptoxide, but of the pentoxide.

---

[1] Pogg. Ann., **138**, 400.

[2] J. prakt. Chem., **90**, 190; Pogg. Ann., **138**, 405.

[3] Pogg. Ann., **138**, 406.

[4] Ber. d. chem. Ges., **6**, 429.

[5] Chem. News, **33**, 35.

[6] J. Chem. Soc., **30**, 469.

[7] Ann. Chem. (Liebig), **198**, 95.

There is no reaction known which offers the slightest evidence that bromine or iodine is capable of directly replacing chlorine in its oxy-acids; indeed, from a theoretical point of view, such a procedure, implying as it does the direct substitution of an element joined to a number of oxygen atoms, is exceedingly improbable. The formation of bromic acid from aqueous hypochlorous acid and bromine, whereas aqueous chloric acid is without action, is due to the tendency of hypochlorous acid to pass over into chloric acid; a conversion which may be assumed to take place through the decomposition of water:

$$HOCl + H_2O = HOClO + H_2;$$
$$HOCl + H_2 = HCl + H_2O;$$
$$HOClO + H_2O = HOClO_2 + H_2;$$
$$HOCl + H_2 = HCl + H_2O.$$

The presence of bromine can only have the effect of favoring the decomposition of water, with the formation of hydrobromic acid, and this acid reacting with hypochlorous acid yields chloride of bromine, which, in the presence of water and chlorine, formed by the interaction of hypochlorous and hydrochloric acids, is converted into bromic acid. As chloric acid does not pass over into perchloric acid nearly as easily as hypochlorous does into chloric acid, the failure of the first acid to induce the indirect oxidation of bromine will be readily understood.

---

[1] Ber. d. chem. Ges., 6, 429.

Another reaction, which seems to imply the replacement of chlorine by bromine or iodine, is the formation of bromic or iodic acid by the action of bromine or iodine on aqueous sodium chlorate, and we are indebted to Potilitzin[1] for the correct interpretation of these changes. This chemist proved that chlorine reacts with sodium bromate, and bromine with sodium chlorate, although much less readily in the last instance, according to the equations:

$$5NaBrO_3 + 3Cl_2 + 3H_2O = 5NaCl + 5HBrO_3 + HClO_3.$$
$$5NaClO_3 + 3Br_2 + 3H_2O = 5NaBr + 5HClO_3 + HBrO_3.$$

Potilitzin particularly emphasizes the fact that these decompositions do not proceed by direct substitution of the halogens. It is obvious that the formation of bromic acid from sodium chlorate is due to the greater affinity of sodium for bromine than for $—OClO_2$; this causes the decomposition, with the intervention of water, and formation of hypobromous acid, which is oxidized to bromic acid. The reaction is essentially of the same character as the formation of sodium bromate from bromine and caustic soda, only it proceeds much less readily, as sodium chlorate represents a much better neutralized sodium derivative than the alkali.

In the preparation of chlorine heptoxide we have found that the danger of explosion may be decidedly reduced by several slight modifications of our former directions.[2] In the first place, it is advisable, especially during warm weather, to keep the retort containing the phosphorus pentoxide at a lower temperature than —10° C., during the addition of perchloric acid, and for some hours afterwards. Instead of heating the retort gradually to 85° C. in a water-bath, it is better to heat slowly, and after two hours remove the heptoxide from the receiver, when about two-thirds of the amount formed has passed over; then four hours longer, at the same temperature, and finally to 85° C., when the last traces of heptoxide are driven off.

---

[1] Ber. d. chem. Ges., **20**^{111}, 777.

[2] This JOURNAL, **23**, 445.

Iodine and chlorine heptoxide usually react in the cold, and if the substances are in a sealed tube a dangerous explosion will probably ensue, which may be avoided to a considerable extent by adhering to the following directions: Pure and finely powdered iodine is brought into a tube sealed at one end, of a diameter of about an inch and a half, and the open end drawn out so as to admit the almost capillary stem of a funnel. The tube is then placed in a freezing mixture and the freshly prepared chlorine heptoxide introduced, in the proportion of an atom of iodine to a molecule of the heptoxide. At this stage of the operation there seems to be but little danger of an explosion, but it is well to seal the tube at once and place it, kept in the freezing-mixture, in a dark closet, where no damage will be done by an explosion. A very energetic action soon takes place, with the liberation of heat, and formation of a white solid. After standing twelve hours about two-thirds of the iodine has been converted into the white compound, and the tube, after opening the sealed end to allow the greenish gas that has been formed to escape, and resealing, is put in a bottle of water and exposed to bright sunlight until the iodine has completely disappeared. This takes from two days to a week. It is well to open the pointed end of the tube several times, as the danger of explosion is thereby materially lessened.

The contents of the tube consisted of a whitish powder, which fumed in the air. When heated to 100° C. in a vacuum, an oily liquid came off, which, taken up in water, gave reactions for perchloric acid, and the solid residue gave all the tests for iodine pentoxide. A portion was dissolved in water, precipitated by silver nitrate, and the silver salt dried to constant weight:

0.4791 gram salt gave 0.3987 gram AgI.

	Theory for $AgIO_3$.	Found.
AgI	83.03	83.22

The action of anhydrous perchloric acid on iodine is much less energetic than that of chlorine heptoxide, and the experiment may be done as described with the heptoxide without danger of explosion. The iodine (0.5 atom of the element to 1 molecule acid) dissolved in the acid, and, after keeping the tube for a day in a dark place, it was exposed to bright sunlight. Oxidation soon began, even in the dark, but it required, at winter temperature, several weeks before the iodine had disappeared, unless the tube was exposed to sunlight, when the oxidation proceeded more rapidly. The product is a moist, pinkish, crystalline powder. It was heated in a vacuum, when a yellowish body remained, consisting of small homogeneous needles. This substance is extremely hygroscopic and rapidly turns black on exposure to the air, owing to the liberation of iodine. When the substance is heated, iodine is given off and a white residue remains, which, as it is converted into iodic acid by dissolving in water, evidently consists of iodine pentoxide. In contact with water it is immediately decomposed with the liberation of iodine and formation of iodic acid.

0.2042 gram substance, dried to constant weight at 70° C. in a vacuum, gave 0.1670 gram free iodine when treated with water.

	Theory for HI_7O_8.	Found.
I_6	81.2	81.7

This substance is interesting from several points of view. In the first place, it is formed in the presence of a considerable excess of perchloric acid, with long exposure to sunlight, and, nevertheless, represents the final stage of the oxidation of iodine, under these conditions. It would further seem to prove that the molecule of solid iodine contains a far greater number of atoms than two, and its slow oxidation causes only a partial breakdown of this large molecule. This behavior of iodine towards slow and rapid oxidation is comparable to the action of chlorine and that of the less energetic iodine on the tetratomic phosphorus molecule, inasmuch as by the last reaction a phosphorus derivative containing two atoms of the element in its molecule may be obtained.[1]

---

[1] There is no direct proof of the presence of hydrogen in this compound, and it may consist only of iodine and oxygen. The above study of the behavior of iodine

Kaemmerer,[1] in his supposed conversion of perchloric into periodic acid, heated a concentrated solution of the first acid with iodine. We tried to repeat this experiment by heating iodine with a pure and concentrated perchloric acid (1.57 sp. gr.) in a flask, whose long neck was enclosed as a condenser. After heating a short time a reaction took place, and the oxidation was then soon completed. The white crystalline substance was filtered under pressure, washed with a little water, then recrystallized, and proved to be iodic acid. An analysis of the silver salt gave the following result :

0.4679 gram dry silver salt gave 0.3916 gram AgI.

	Theory for $AgIO_3$.	Found.
AgI	83.03	83.61

We then varied the experiment by taking perchloric acid of different strengths, and the conditions of temperature, but in all cases a similar result was obtained ; that is, iodic acid was formed. We were also unable to detect the presence of periodic acid in the mother-liquors from the iodic acid, and we do not hesitate to state that the formation of periodic from perchloric acid, as described by Kaemmerer, is incorrect.

Bromine and chlorine heptoxide may be exposed for weeks in a sealed tube to sunlight without any reaction taking place, even in presence of a very large excess of oxide. Nor did we notice an action between anhydrous perchloric acid and bromine, when they were exposed, in a sealed tube, for a long time to sunlight, or on warming the tube. We were equally unable to oxidize bromine by boiling it a long time with a concentrated solution of perchloric acid.

It is not easy to understand the confidence which is still placed in the above investigations of Kaemmerer, as a very considerable portion of the work has been experimentally disproved, and its character, mostly mere statements, unaccompanied by any

---

towards perchloric acid is preliminary, and the substance will be more fully analyzed and examined. Several oxides of iodine—$I_{10}O_{19}$ and I_3O_{13}— containing a number of iodine atoms to the molecule, and obtained by moderate oxidation of the element—have been previously described, but their existence is now considered doubtful. In view of the important theoretical bearing of the subject, the behavior of iodine, as well as that of some other elements, towards the slow action of perchloric and nitric acids and other oxidizers will be studied.

[1] Pogg. Ann., 138, 406.

quantitative evidence, hardly seemed to have invited it. It is to be hoped, however, that such gross errors as the existence of perbromic acid, or the direct substitution of chlorine or bromine in their oxy-acids by iodine, which find a place in most text-books, even though of very elementary character, will soon be consigned to the oblivion, which they have long merited.

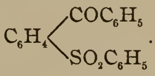
TUFTS COLLEGE, MASS.

ORTHOPHENYLSULPHONEBENZOIC ACID AND RELATED COMPOUNDS.[1]

BY HALL CANTER.

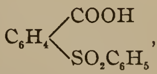
Introduction.

Working in this laboratory Newell[2] undertook an investigation, the primary object of which was to make and study orthobenzoyldiphenylsulphone,



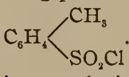
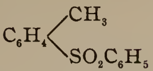
$$C_6H_4\left\langle\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}\right. .$$

He commenced his work in the para series and met with results so satisfactory as to cause him to confine his work to that series. The research recorded in these pages was begun with the intention of preparing and studying orthophenylsulphonebenzoic acid,



$$C_6H_4\left\langle\begin{matrix}COOH\\SO_2C_6H_5\end{matrix}\right. ,$$

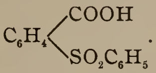
and compounds derived from it.

The substance that served as a starting-point in the work was orthotoluenesulphone chloride,  $C_6H_4\left\langle\begin{matrix}CH_3\\SO_2Cl\end{matrix}\right.$. By subjecting this to the Friedel-Crafts reaction, employing benzene and aluminium chloride, it was thought possible to pass to orthotolylphenylsulphone,  $C_6H_4{<}\begin{matrix}CH_3\\SO_2C_6H_5\end{matrix}$; then by means of a suitable oxidizing agent to transform the methyl group into carboxyl and obtain orthophenylsulphonebenzoic acid,

---

[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1900, for the degree of Doctor of Philosophy.

[2] This JOURNAL, 20, 302.

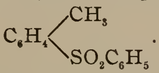


$$C_6H_4{<}\begin{matrix}COOH\\SO_2C_6H_5\end{matrix}.$$

Preparation of Material.

The orthotoluenesulphone chloride employed was a kilogram presented to Professor Remsen by the chemical factory of von Heyden.[1] This was filtered from a small quantity of solid material contained in it, and then used. The benzene was redistilled and thoroughly dried. The chloride of aluminium was the fresh commercial article obtained from the laboratory.

Orthotolylphenylsulphone,



$$C_6H_4{<}\begin{matrix}CH_3\\SO_2C_6H_5\end{matrix}.$$

The isomeric paratolylphenylsulphone has been prepared by several methods, among others that of Beckurts and Otto,[2] who employed toluene, aluminium chloride, and benzenesulphone chloride. A method perfectly analogous to this, and the same as that employed by Newell,[3] was made use of in preparing orthotolylphenylsulphone. The following directions were found to be satisfactory:

For each 25 gram portion of orthotoluenesulphone chloride 100 grams of benzene and 30 grams of aluminium chloride were used. The amount of toluenesulphone chloride employed was varied up to 40 grams, the proportion of benzene and aluminium chloride being the same. Though the reaction progressed apparently well, yet the yield of orthotolylphenylsulphone was not proportionately increased, and the sulphone chloride was always used in portions of 25 grams. Orthotoluenesulphone chloride easily dissolves in benzene at a slightly elevated temperature, forming a solution of dark wine color. Aluminium chloride is added in 8 or 10 portions during an hour. Upon addition of the first portion reaction begins, and gradually becomes more energetic. A temperature of 75° causes the reaction to proceed smoothly, yet rapidly, so the flask containing the mixture was kept in a water-bath at this temperature. When three-fourths of the aluminium chloride has been added, reaction becomes less violent with each subsequent addition; and when all the aluminium chloride has been added, the temperature of the water-bath is kept at 80° to 85° till the evolution of hydrochloric acid ceases. The liquid in the flask at this stage has become darker, and is now poured into a large beaker containing tepid water to which a little hydrochloric acid has been added. The liquid must be added slowly to the water and stirred constantly; otherwise sufficient heat is generated by the action of water on undecomposed aluminium chloride to cause partial evaporation of the benzene—a thing not desirable at this stage. On top of the water appears the layer of benzene containing the product of the reaction in solution. This is separated, passed through a filter, again washed with water to remove any chloride of aluminium, and then dried. Most of the benzene is distilled off, and the remaining portion is evaporated from a beaker on the water-bath. The crude sulphone solidifies, showing a crystalline structure, and this hardening can be quickened by stirring with a glass rod. The hardened, dark-brown mass is dissolved in 95 per cent alcohol and filtered from a small quantity of insoluble matter. To remove the color the solution in alcohol is boiled several times with animal charcoal. A considerable amount of the sulphone remains behind with the charcoal, and several treatments with boiling alcohol are necessary to recover all of it. Orthotolylphenylsulphone crystallizes in white leaflets that melt at 67°.5 to 68° (uncorr.). It is easily soluble in petroleum ether, ordinary ether, benzene, alcohol, glacial acetic acid, and to a very slight degree in water. It is dissolved by strong nitric acid, from which it can be recovered by adding water; insoluble in hydrochloric acid. Upon analysis the following results were obtained:

---

[1] I beg here to express my hearty thanks to the officers of the von Heyden factory for their liberality in furnishing the material, and for other courtesies.—I. R.

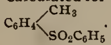
[2] Ber. d. chem. Ges., 11, 2068.

[3] *Loc. cit.*

I. 0.1831 gram substance gave 0.4488 gram CO_2 and 0.0877 gram H_2O.

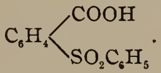
II. 0.2207 gram substance gave 0.5423 gram CO_2 and 0.1063 gram H_2O.

III. 0.1333 gram substance gave 0.1349 gram $BaSO_4$.

	Calculated for	Found.	
	 $C_6H_4\begin{cases}CH_3\\SO_2C_6H_5\end{cases}$.	I.	II.
C	67.24	66.85	67.01
H	5.18	3.33	5.35
S	13.81	13.91	....

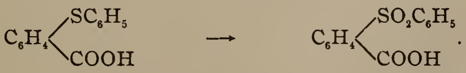
The determinations of carbon and hydrogen were made by the lead chromate method of de Roode, and the sulphur by the method of Carius.

Orthophenylsulphonebenzoic Acid,



$$C_6H_4\begin{cases}COOH\\SO_2C_6H_5\end{cases}.$$

Graebe and Schulteiss[1] claim to have made this acid in 1891. In the course of an investigation carried out by them they treated phenylthiosalicylic acid with strong nitric acid. The reaction-product, when brought into water, formed an oil, which solidified upon standing. Purified by ether and crystallized from 90 per cent alcohol, their new acid appeared in the form of white needles, containing 1 molecule of water of crystallization and melting at 99°. When heated to 105° this water is lost and the acid then melts at 152°. They called the substance sulphobenzidorthocarbonic acid. The relation to phenylthiosalicylic acid is seen thus:



$$C_6H_4\begin{cases}SC_6H_5\\COOH\end{cases} \longrightarrow C_6H_4\begin{cases}SO_2C_6H_5\\COOH\end{cases}.$$

In this investigation orthotolylphenylsulphone was subjected to the action of oxidizing agents. In the first instance chromic acid was tried. A small quantity of the sulphone was dissolved in glacial acetic acid in a flask attached to a return-condenser, and to this solution was added chromic acid in glacial acetic acid. The flask was then heated a sufficiently long time and the product examined. This method was abandoned, as a relatively small amount of acid was thus obtained. Potassium permanganate was used as the oxidizing agent and the process in detail was as follows :

---

[1] Ann. Chem. (Liebig), **263**, 7.

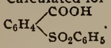
Ten grams of orthotolylphenylsulphone were suspended and partially dissolved in 2.5 liters of boiling water. Into the flask, steam was continuously conducted to prevent bumping and to keep the water hot. Finely powdered potassium permanganate in quantity slightly in excess of the calculated amount was added in small spoonfuls throughout the space of an hour and a half. The boiling was continued for fifteen hours, till the contents of the flask became quite black, and a small portion removed and filtered appeared quite clear. A few cubic centimeters of alcohol were added, the liquid was filtered from the manganese dioxide and evaporated to the volume of 1 liter. Upon addition of hydrochloric acid the acid was precipitated as a white flocculent mass. If precipitated from a cold solution it shows more of a crystalline structure. The acid was crystallized from alcohol, but it was hardly possible to obtain it pure in this way, because of the presence of some unchanged sulphone. The barium salt of the acid was made, but even this carried with it some sulphone. The solution of the barium salt was then evaporated to dryness, and the dry salt was treated several times with boiling alcohol. In this manner the remaining small portions of the sulphone were removed. The remaining barium salt was recrystallized, and from this the free acid was obtained. This was purified by recrystallization from ordinary alcohol.

Orthophenylsulphonebenzoic acid crystallizes in clear small plates, frequently grouped in clusters. It is insoluble in water and readily soluble in alcohol. A portion heated for an hour and a half in an air-bath, at a temperature of 130°, lost nothing in weight. The acid, as above obtained, melts at 267° to 268° (uncorr.).

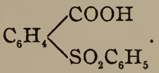
Analysis :

0.2064 gram substance gave 0.4480 gram CO_2 and 0.07709 gram H_2O.

0.2625 gram substance gave 0.2346 gram $BaSO_4$.

	Calculated for  $C_6H_4<^{COOH}_{SO_2C_6H_5}$.	Found.
C	59.54	59.20
H	3.82	4.15
S	12.21	12.28

Salts of Orthophenylsulphonebenzoic Acid,



$C_6H_4<^{COOH}_{SO_2C_6H_5}$.

In addition to the analysis of the acid several salts were made, the analysis of which confirms the structure above assigned the acid.

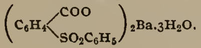
Barium Salt.—The salt is readily soluble in water and crystallizes from moderately concentrated solutions in clear, white needles, some being 15 mm. in length. If the solution is too concentrated the salt appears in the form of granular nodules. Upon analysis the following results were obtained :

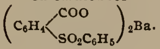
0.1560 gram salt, heated to 160° for an hour, lost 0.0118 gram H_2O.

0.1560 gram salt gave 0.0507 gram $BaSO_4$.

0.1972 gram salt at 160° lost 0.0151 gram H_2O.

0.1972 gram salt gave 0.0639 gram $BaSO_4$.

	Calculated for	Found.	
	 $\left(C_6H_4<^{COO}_{SO_2C_6H_5}\right)_2Ba.3H_2O$.	I.	II.
H_2O	7.57	7.56	7.65

	Calculated for	Found.	
	 $\left(C_6H_4<^{COO}_{SO_2C_6H_5}\right)_2Ba$.	I.	II.
Ba	20.81	20.68	20.64

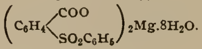
Magnesium Salt.—This salt was made by adding to a solution of the barium salt a solution of pure magnesium sulphate in quantity just sufficient to precipitate the barium present. The salt is easily soluble in water and crystallizes from it in the form of short, silken needles, which show a tendency to arrange themselves in clusters. Results of analyses were as follows :

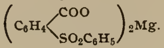
0.1827 gram salt lost 0.0383 gram H_2O below 160°.

0.1827 gram salt gave 0.0320 gram $MgSO_4$.
0.1618 gram salt lost 0.0339 gram H_2O below 160°.
0.1618 gram salt gave 0.0293 gram $MgSO_4$.

A third determination of water of crystallization was made with some of the same salt that had been dried between filter-paper for several days.

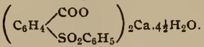
0.1038 gram salt lost 0.0215 gram H_2O below 160°.

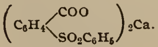
	Calculated for  $\left(C_6H_4{<}\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Mg.8H_2O$.	Found. I.	II.	III.
H_2O	20.86	20.96	20.95	20.71

	Calculated for  $\left(C_6H_4{<}\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Mg$.	Found. I.	II.
Mg	4.39	4.40	4.55

Calcium Salt.—This is very easily soluble in water and crystallizes from it in short needles, almost wholly grouped in clusters. Upon analysis the following results were obtained:

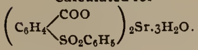
0.1595 gram salt lost 0.0206 gram H_2O below 160°.
0.1595 gram salt gave 0.0333 gram $CaSO_4$.
0.1452 gram salt lost 0.0186 gram H_2O below 160°.
0.1452 gram salt gave 0.0306 gram $CaSO_4$.

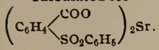
	Calculated for  $\left(C_6H_4{<}\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Ca.4\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	12.62	12.91	12.81

	Calculated for  $\left(C_6H_4{<}\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Ca$.	Found. I.	II.
Ca	7.11	7.05	7.10

Strontium Salt.—This salt is easily soluble in water and crystallizes in small leaflets or flakes. Analysis resulted as follows:

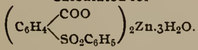
0.1789 gram salt lost 0.0143 gram H_2O below 160°.
0.1789 gram salt gave 0.0494 gram $SrSO_4$.
0.1232 gram salt lost 0.0099 gram H_2O.
0.1232 gram salt gave 0.0343 gram $SrSO_4$.

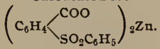
	Calculated for	Found.	
	 $\left(C_6H_4<^{COO}_{SO_2C_6H_5}\right)_2Sr.3H_2O.$	I.	II.
H_2O	8.13	7.99	8.03

	Calculated for	Found.	
	 $\left(C_6H_4<^{COO}_{SO_2C_6H_5}\right)_2Sr.$	I.	II.
Sr	14.35	14.28	14.47

Zinc Salt.—To the acid suspended in water an excess of pure zinc oxide was added. The flask containing the substance was attached to a return-condenser, and the contents heated to boiling for two hours. After standing in dilute solution over night, a few crystals of the salt appeared in the form of short, glistening needles; but to procure the salt in quantity sufficient for analysis, the solution was evaporated to a small volume.

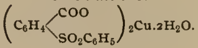
0.1678 gram salt lost 0.0138 gram H_2O.
0.1678 gram salt gave 0.0418 gram $ZnSO_4$.
0.1592 gram salt lost 0.0132 gram H_2O.
0.1592 gram salt gave 0.0398 gram $ZnSO_4$.

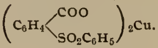
	Calculated for	Found.	
	 $\left(C_6H_4<^{COO}_{SO_2C_6H_5}\right)_2Zn.3H_2O.$	I.	II.
H_2O	8.42	8.22	8.29

	Calculated for	Found.	
	 $\left(C_6H_4<^{COO}_{SO_2C_6H_5}\right)_2Zn.$	I.	II.
Zn	11.11	10.97	11.15

Copper Salt.—In a flask attached to a condenser the free acid and the copper oxide were boiled together and the solution of the copper salt filtered off. Immediately upon cooling some of the salt separated out from the dilute solution, but during the night there was no increase in amount, and the solution was evaporated in stages till the salt crystallized more abundantly. It is not easily soluble in water, and crystallizes either in small plates or in the form of a powder. The salt is dark-green in color, and after losing its water of crystallization it turns light-blue. Trouble was had in the first trials to determine the amount of water contained, as the salt decomposes below 160°. Analysis resulted as follows:

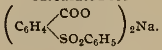
0.1488 gram salt lost 0.009 gram H_2O.
0.1488 gram salt gave 0.0186 gram CuO.

	Calculated for  $\left(C_6H_4\left\langle\begin{array}{l}COO\\SO_2C_6H_5\end{array}\right.\right)_2Cu.2H_2O.$	Found.
H_2O	5.79	6.04

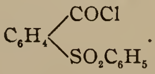
	Calculated for  $\left(C_6H_4\left\langle\begin{array}{l}COO\\SO_2C_6H_5\end{array}\right.\right)_2Cu.$	Found.
Cu	10.81	10.62

Sodium Salt.—This salt was prepared from the barium salt, instead of employing the free acid and sodium carbonate. To a solution of the barium salt a dilute solution of sodium sulphate is slowly added till all the barium present is just precipitated. The salt is exceedingly easily soluble in water. After standing more than two months in a desiccator it crystallized from a syrupy solution in fine silken needles. Shaking the beaker causes them partially to dissolve. The following analyses were made of the dry amorphous salt:

0.1409 gram salt gave 0.0357 gram Na_2SO_4.
0.1521 gram salt gave 0.0375 gram Na_2SO_4.

	Calculated for  $\left(C_6H_4\left\langle\begin{array}{l}COO\\SO_2C_6H_5\end{array}\right.\right)_2Na.$	Found. I.	 II.
Na	8.09	8.21	7.98

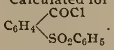
Orthophenylsulphonebenzoyl Chloride,



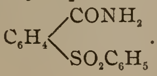
$$C_6H_4\left\langle\begin{array}{l}COCl\\SO_2C_6H_5\end{array}\right..$$

This compound can be made either by treating a salt of orthophenylsulphonebenzoic acid, preferably the sodium salt, with phosphorus pentachloride, or by treating the free acid with the same reagent. The latter method was employed. A quantity of the acid was mixed with a slight excess of pentachloride of phosphorus in an evaporating dish, and the two were rubbed together with a pestle. At ordinary temperature the substances react slightly, and when heated to 45° on the water-bath the reaction proceeds rapidly, the whole mass becoming semi-liquid, or else granular, in structure. The dish was then placed in a sulphuric-acid bath and heated for two hours at a temperature of 200°. In this way most of the oxychloride of phosphorus was expelled, while a slight evolution of hydrochloric acid was noticed so long as the heating was continued. Upon cooling, the substance solidifies to a dark-gray mass. Tepid water was added, the solid mass powdered into granular form, washed several times with cold water by shaking, and finally treated several times with water upon the filter-pump, and then dried between filter-paper. Orthophenylsulphonebenzoyl chloride is very difficultly soluble in boiling petroleum ether of 105° to 130°; difficultly soluble in absolute ether, from which it crystallizes in small, thin, clear plates; more readily, though not easily, soluble in boiling benzene, from which, upon evaporation, it crystallizes in plates. The most satisfactory solvent is glacial acetic acid, in which the chloride is easily soluble. From this it crystallizes in short needles arranged in clusters. After repeated crystallizations the chloride melted at 262°.5 to 263°.5. The isomeric para compound is slightly volatile, but the ortho chloride exhibits no such property. Some of the substance—0.1120 gram—that had been thoroughly dried and kept in a glass bottle, was heated gradually as high as 145°, but there was no loss in weight. A small quantity of the chloride was placed in a flask with cold water and shaken repeatedly. After standing for twenty-four hours there was slight decomposition, as indicated by silver nitrate. When boiled with water the chloride is quickly decomposed. A determination of chlorine in this way resulted as follows:

0.1756 gram chloride gave 0.8833 gram AgCl.

	Calculated for  $C_6H_4\left<\begin{matrix}COCl\\SO_2C_6H_5\end{matrix}\right.$.	Found.
Cl	12.62	12.45

Orthophenylsulphonebenzamide,

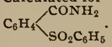


$$C_6H_4\left<\begin{matrix}CONH_2\\SO_2C_6H_5\end{matrix}\right. .$$

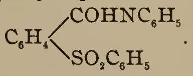
Pure orthophenylsulphonebenzoyl chloride was placed in a suitable flask and covered with strong ammonia. The vessel was kept at ordinary temperature, and vigorously shaken at intervals throughout twenty-four hours. There was no change apparent at the end of this time, except that some of the substance seemed to have passed into solution. The vessel was then placed in a water-bath, slightly evaporated, and allowed to stand over night, when the reaction-product appeared as a light crystalline powder. It is easily soluble in alcohol, and from this solution crystallizes in beautifully, regular, transparent plates. When the determination of the melting-point was made, the substance melted through a range of several degrees. After numerous crystallizations the same thing occurred, the melting beginning at about 220° and continuing up to 257°. At the same time a deposit was noticed on the glass in the upper part of the melting-point tube, evidently the sublimed amide. Another portion of the substance was then placed in a tube and both ends were sealed. Heated in an acid-bath the substance then melted at 245° to 255°. Analysis for nitrogen was made by the absolute method of Dumas, and the sulphur was determined by Liebig's method.

0.1844 gram amide gave 8.4 cc. = 0.0097 gram N under standard conditions.

0.1528 gram amide gave 0.1388 gram $BaSO_4$.

	Calculated for  $C_6H_4\left<\begin{array}{l}CONH_2\\SO_2C_6H_5\end{array}\right.$.	Found.
N	5.37	5.26
S	12.27	12.48

Orthophenylsulphonebenzanilide,



$$C_6H_4\left<\begin{array}{l}COHNC_6H_5\\SO_2C_6H_5\end{array}\right..$$

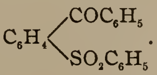
Some of this compound was made in two ways: Orthophenylsulphonebenzoyl chloride was dissolved in benzene and aniline was added in small portions, with continued shaking of the flask. Water was added to dissolve the aniline hydrochloride, and the anilide was subsequently purified. The following method was employed in making the anilide in quantity: An emulsion of aniline and water was made by vigorously shaking the two, aniline being employed in quantity representing 2 molecules for each one of the chloride to be used. Orthophenylsulphonebenzoyl chloride was finely powdered and added in small portions to the emulsion, the flask being shaken after each addition. Reaction takes place when the first portion of the chloride has been added, a grayish-brown, gummy substance appearing upon the surface of the liquid. The flask was shaken at intervals through two days, after which the anilide appeared as a finely divided, granular mass at the bottom of the vessel. This was filtered off and washed several times with dilute hydrochloric acid and then with water. It was dissolved in 95 per cent alcohol and treated twice with animal charcoal, but the solution always remained slightly colored. From alcohol the anilide crystallizes readily in small glistening plates, which melt at 234° to 235° (uncorr.). The estimations of nitrogen and sulphur were made as in the case of the amide, and gave the following results:

0.3122 gram anilide gave 10.8 cc. = 0.01238 gram N under standard conditions.

0.1602 gram anilide gave 0.1119 gram $BaSO_4$.

	Calculated for $C_6H_4\begin{cases} COHNC_6H_5 \\ SO_2C_6H_5 \end{cases}$.	Found.
N	4.16	3.96
S	9.48	9.59

Orthobenzoyldiphenylsulphone,

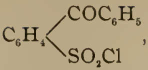


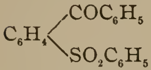
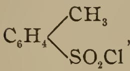
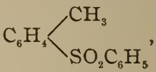
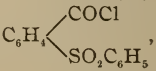
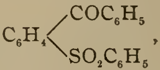
$$C_6H_4\begin{cases} COC_6H_5 \\ SO_2C_6H_5 \end{cases}.$$

This compound was made in this laboratory by Remsen and Saunders,[1] who were working upon the chlorides of orthosulphobenzoic acid. By treating a mixture of these chlorides with benzene and aluminium chloride they obtained in the first instance a compound of the supposed structure

---

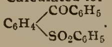
[1] This JOURNAL, 17, 362.


$C_6H_4{<}\begin{matrix}COC_6H_5\\ SO_2Cl\end{matrix}$,

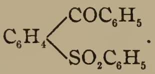
which they called orthobenzoylbenzenesulphone chloride. They obtained the same compound by treating the solid chloride of orthosulphobenzoic acid with benzene and aluminium chloride. By continued treatment of the mixed chlorides, as above, the intermediate substance first formed passes over to  $C_6H_4{<}\begin{matrix}COC_6H_5\\ SO_2C_6H_5\end{matrix}$. To see whether or not the benzoyldiphenylsulphone above formed possesses the structure assigned to it, the method of making it in this investigation was brought into account. Starting with orthotoluenesulphone chloride,  $C_6H_4{<}\begin{matrix}CH_3\\ SO_2Cl\end{matrix}$, introducing the phenyl group,  $C_6H_4{<}\begin{matrix}CH_3\\ SO_2C_6H_5\end{matrix}$, oxidizing and then passing to the chloride,  $C_6H_4{<}\begin{matrix}COCl\\ SO_2C_6H_5\end{matrix}$, and then introducing another phenyl group,  $C_6H_4{<}\begin{matrix}COC_6H_5\\ SO_2C_6H_5\end{matrix}$, there seems only one possible structure for orthobenzoyldiphenylsulphone. Its method of formation was as follows: Ten grams of orthophenylsulphonebenzoyl chloride were dissolved in benzene in a tubulated retort attached to a return-condenser. At ordinary temperature reaction did not take place upon the addition of aluminium chloride, and the water-bath in which the retort was placed was raised to 65°. After one-half hour the solution turned dark-red. When all the chloride of aluminium—12 grams—had been added, the contents of the vessel became quite dark, and the temperature was kept at 80° till hydrochloric acid ceased to be evolved. The introduction of the second phenyl group into the chloride seemed harder to accomplish than that of the first. When thereaction was completed the retort was slowly emptied into a large beaker of water, to which a little hydrochloric acid had been added. Considerable heat was generated, the water became milky, and the benzene arose to the surface, forming a dark-colored layer upon the water. This was separated, and the water treated several times with benzene. All the benzene was then filtered, thoroughly washed, and dried. Upon standing over night some crystals separated from the dilute solution. These were dissolved; most of the benzene was distilled off, and the remainder evaporated upon a water-bath, leaving the new compound in the form of a dark-brown crystalline substance. This was dissolved in alcohol, animal charcoal was added, and the solution was heated to boiling for several minutes. From the filtered solution orthobenzoyldiphenylsulphone quickly crystallizes in thin plates or leaflets, being difficultly soluble in alcohol. It is more easily soluble in benzene, from which it crystallizes in flakes, as in the first instance. The purified substance melted at 183° to 184°. The crystals are stable in the air ; they are not readily acted on by alcoholic potash ; they can be dissolved in warm, strong, nitric acid, and again recovered by addition of water ; strong hydrochloric acid has no effect upon them. Analysis for carbon and hydrogen by de Roode's method, and for sulphur by the method of Liebig gave the following results :

0.1660 gram substance gave 0.4288 gram CO_2 and 0.0658 gram H_2O.

0.1511 gram substance gave 0.1047 gram $BaSO_4$.

	Calculated for  $C_6H_4{<}^{COC_6H_5}_{SO_2C_6H_5}$.	Found.
C	70.78	70.45
H	4.35	4.40
S	9.95	9.52

Orthobenzoyldiphenylsulphone was fused with an excess of potassium hydroxide, the heat being gradually intensified. When the substance begins to melt, some volatile substance escapes, and this fact probably accounts for the low determination in the case of the sulphur. Gradually the melting continues till the benzoyldiphenylsulphone forms with the molten potassium hydroxide a tranquil, dark straw-colored liquid, and this cools to a yellow-brown mass. When treated once or twice with hot water this partially dissolves, leaving a small insoluble residue behind. The filtered water solution, when treated with hydrochloric acid, gave a precipitate of benzoic acid, as determined by the melting-point. An accident caused the loss of the insoluble portion. However, the identical properties of this substance, its similar behavior on fusion, the presence of benzoic acid in the filtrate after treating the fused mass with water, leave no doubt as to its being the same substance as that obtained by Remsen and Saunders from the solid chloride of orthosulphobenzoic acid, while the method of formation and the analysis prove that it has the structure



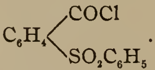
$$C_6H_4\left<\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}\right..$$

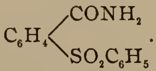
Conclusion.

The results obtained in this investigation may be summarized thus :

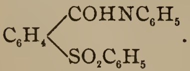
1. By subjecting orthotoluenesulphone chloride to the Friedel-Crafts reaction, it readily passes into orthotolylphenylsulphone.

2. Employing potassium permanganate, this can be oxidized to orthophenylsulphonebenzoic acid, which forms well characterized salts.

3. By means of phosphorus pentachloride the acid can be converted into the chloride,  $C_6H_4\left<\begin{matrix}COCl\\SO_2C_6H_5\end{matrix}\right..$

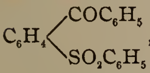
4. When treated with concentrated ammonia for twenty-four hours at ordinary temperature, the chloride yields an amide of the structure  $C_6H_4\left<\begin{matrix}CONH_2\\SO_2C_6H_5\end{matrix}\right..$

5. If to an emulsion of aniline and water orthophenylsulphonebenzoyl chloride is added, there is formed the anilide,



$$C_6H_4\left<\begin{matrix}COHNC_6H_5\\SO_2C_6H_5\end{matrix}\right..$$

6. By treating the chloride with benzene and aluminium chloride, another phenyl group can be introduced, though not

so readily as in the case of orthotoluenesulphone chloride. The new substance thus formed is orthobenzoyldiphenylsulphone, and is the same as that obtained by Remsen and Saunders by treating the chlorides of orthosulphobenzoic acid with benzene and aluminium chloride. Its structure is  $C_6H_4<\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}$, and in properties it differs markedly from the isomeric para-compound.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXVIII.—ON THE IMPORTANCE OF FORMIC ALDEHYDE AS A PRODUCT OF THE PARTIAL COMBUSTION OF ORGANIC COMPOUNDS.

By S. P. Mulliken, with J. W. Brown and P. R. French.

It has been shown elsewhere in this Journal[1] by Mulliken and Scudder that formic aldehyde is apparently one of the most common products of the partial combustion of organic compounds by hot copper oxide, and that its appearance in minute traces as a result of such combustions ought never to be accepted as sufficient proof that the substance burned contains a methoxyl group. These conclusions were based entirely on qualitative experiments made incidentally in connection with a study of certain color tests for methyl alcohol. The present investigation is quantitative in character. Its object is to furnish direct proof that the quantities of formic aldehyde which may be obtained from the oxidation of various typical and purified non-methoxylated compounds are, in general, greater than could arise from accidental impurities in the substances used.

Before proceeding to a description of these experiments, allusion should be made to the few scattering earlier investigations which have a more or less direct bearing on the matter under consideration. Legler[2] claims to have found formic

Vol. **24**, p. 446. Attention is here called to two slight corrections that should be made in the text of the article quoted. On page 451, line 21, insert the words "*containing strong sulphuric acid*," between "second tube" and "held"; and on p. 452, line 18, read "*tertiary*," between "secondary" and "and butyl."

[2] Ann. Chem. (Liebig), **217**, 382; Ber. d. chem. Ges., **18**, 3343.

aldehyde in small quantities among the products of the phosphorescent combustion of ethyl ether in presence of metallic platinum. Pratesi[1] obtained it from a decomposition of the vapors of boiling ethyl nitrate induced by a strip of incandescent platinum. Its formation was detected by Schützenberger,[2] when ethylene was heated with oxygen to 400°; and by Wolkow and by Menschutkin,[3] when a mixture of trimethylene and air was passed through a red-hot tube. Its occurrence to the extent of 0.5 per cent in wood smoke, which has lately been noted by Pasqualis,[4] may also be mentioned, although its appearance in this case is no doubt due merely to a secondary oxidation of the methyl alcohol, which is always formed when wood is subjected to destructive distillation.

In our experiments the oxidations were all made by means of the well-known, simple and efficient apparatus devised by Loew[5] for the preparation of formic aldehyde from methyl alcohol. Loew early used this apparatus for the partial oxidation of several non-methoxylated substances. Ethyl ether, ethyl acetate, and ethylamine, all gave him acetaldehyde, while toluene yielded some benzaldehyde; but no substance other than methyl alcohol is mentioned as having given formic aldehyde, means for detecting small quantities of formic aldehyde in the presence of much acetic aldehyde being at that time unknown.

In Loew's method a stream of dry air, more or less fully saturated with a combustible vapor, is aspirated through a long tube of infusible glass containing a short coil of oxidized copper gauze, the latter being first brought nearly to redness by the temporary application of a gas flame. The copper oxide of the roll serving as an oxygen carrier, the roll continues to glow brightly, after the gas flame is withdrawn, as long as the combustible mixture is supplied. The liquefiable products of the reaction are condensed by passage through a series of well-cooled bottles containing water, which are interposed between the combustion tube and the suction-pump.

---

[1] Gazz. chim. ital., **14**, 221.

[2] Bull. Soc. Chim., **31**, 482.

[3] Ber. d. chem. Ges., **31**, 3067.

[4] Centrbl., 1897, II., 1012.

[5] J. prakt. Chem., **33**, 324; cf. also Tollens in Ber. d. chem. Ges., **19**, 2135.

In our work the suction was supplied by a single Richards' water aspirator run at nearly its full capacity. The combustion tube was 2 feet long and supported near its lower end by a clamp protected by asbestos. The copper roll, 2 inches in length, was made of fine-meshed gauze rolled loosely to fill the whole bore of the tube. The space within the tube above the coil was filled with fibrous asbestos, as a precaution against possible explosions, though none ever occurred.

The aspirated air, after being first dried by sulphuric acid, was passed rapidly through the liquid with whose vapors it was to be charged. The liquid was placed in a round-bottomed flask supported at such a height that a water-bath might be brought under it to raise the temperature, if desired. An exit-tube passing through the stopper of this flask conveyed the mixture of air and vapor into the combustion tube. The latter was drawn out and bent at its lower end so as to just dip beneath the surface of 50 cc. of distilled water in the first of a series of four condensing bottles, each of which also contained water through which the gaseous combustion products were made to pass. Whenever a new vapor was to be burned, some preliminary experimenting was required to find the best temperature at which to maintain the evaporating liquid, and the proper rate at which to draw air through it. After the best conditions had been once ascertained, however, the combustion usually proceeded smoothly and with very little separation of carbon, the copper roll often maintaining its dull-red glow for several hours without requiring any special attention from the experimenter. A few moments' application of a Bunsen burner flame was frequently quite sufficient to start the reaction, though there were cases in which the heating had to be continued for more than fifteen minutes. The ratio between air and vapor in the different experiments could not readily be kept constant, and bore no known relation to the theoretical quantities corresponding to any particular chemical equations. The composition of the mixtures and the rate of aspiration were simply such as experience showed were favorable to uninterrupted combustion. In experiments with the same substance the largest yields of aldehyde were often obtained when only half the roll was glowing.

Considerable time was spent in the search for a reliable analytical method for the determination of small quantities of formic aldehyde in presence of much acetic aldehyde. In the course of this search Mr. Brown studied nearly all the methods that have been proposed for the analysis of formic aldehyde solutions, and came to the conclusion that acetic aldehyde must always first be removed. The method of separation which was adopted was based on the fact, referred to in the article by Mulliken and Scudder, that acetic aldehyde may be completely boiled out from dilute aqueous solutions in such a way that practically all of the formic aldehyde will be held back by the water. To accomplish this result in the present instance, the liquid contents of all the condenser bottles were united, diluted to 500 cc. with water, and placed in a round-bottomed liter flask connected with a long upright return-flow condenser. The upper end of the condenser was joined, by means of a descending glass tube, with a glass worm packed in ice and salt. The worm delivered into a flask surrounded by a freezing-mixture. The dilute aldehyde solution was gently boiled for two hours to drive over the acetic aldehyde. During the boiling, warm water at 45° to 50° was kept circulating through the condenser, the temperature being carefully controlled with the aid of a thermometer hung within the glass condenser-jacket. It was found, by direct experiments, that the quantity of formic aldehyde vapor which passed over and was absorbed by water placed in the cooled receiver upon boiling a 1 per cent aqueous solution for two hours, as above described, was too small to be accurately determined, though its presence in the receiver could be shown qualitatively by the delicate gallic acid test. The removal of acetic aldehyde by the process was so complete that in the experiment on the oxidation of ethyl alcohol, in which 43 grams of acetic aldehyde were produced, no trace of acetic aldehyde could be detected in the flask at the close of the two hours' boiling. A strong, unmistakable formalin odor, was, however, noticeable in each of the warm boiled solutions in which formic aldehyde was determined. These solutions also all gave very pronounced qualitative reactions for formic aldehyde, by the gallic acid, resorcin, and hexamethylenetetramine tetrabromide tests. The determinations of formic aldehyde which follow were made by the colorimetric method of Trillat in essentially the form described by Wolff,[1] though with certain added precautions.

The determinations of acetic aldehyde were obtained by the colorimetric method of Thresh,[2] which was so far modified and improved as to give results which are trustworthy to within 2 per cent of their total value. Acetic aldehyde was tested for in all oxidation-products by adding solid sodic hydrate to a few centimeters of the mixed and diluted aqueous solutions until the liquid became almost syrupy, and then boiling for a minute or two. The least trace of acetic aldehyde then gave the characteristic aldehyde resin odor, and a deep-yellow solution.

The compounds chosen for oxidation were Kahlbaum's best preparations, and were carefully rectified before use by distillation through a tall Le Bel-Henninger tower. Only the middle portion of a large fraction of correct and constant boiling-point was used, unless it is otherwise stated in the record of the experiment. In the following brief statement of results the compounds studied follow one another in an order which corresponds to the quantity of formic aldehyde produced by their respective oxidations, the substance giving the largest yield closing the list. The experiments on acetone and ethyl alcohol were made by Mr. Brown, the remainder by Mr. French.

SUMMARY OF EXPERIMENTAL RESULTS.

Acetone.—(Prepared from the pure bisulphite compound.) 271 grams gave 0.6055 gram formic aldehyde, but no acetic aldehyde. Duration of oxidation, two and a half hours. Temperature of bath, 25° to 30°.—*Yield of formic aldehyde, 0.22 per cent.*

Ethyl Alcohol.—(Prepared from the purest absolute alcohol.) 187 grams gave 0.832 gram formic aldehyde and 42.9 grams acetic aldehyde. Duration of oxidation, three hours. Temperature of bath, 35° to 40°.—*Yield of formic aldehyde, 0.44 per cent.*

---

[1] Ztschr. d. Nahr. u. Genuss., 1890, 89.

[2] Pharm. Jour. (3), 9, 408.

Pentane.—(Boiling-point 35° to 37°.) 119 grams gave 1.05 grams formic aldehyde, but no acetic aldehyde. No bath was employed.—*Yield of formic aldehyae, 0.88 per cent.*

Acetic Acid.—("99 to 100 per cent 'Kahlbaum's acid' free from homologues".) 232 grams with the bath at 60° to 65° gave 1.95 grams formic aldehyde, but no acetic aldehyde. The oxidation was very easily controlled and the copper roll no more disintegrated than in other experiments. Most of the unoxidized acid in the distillate was neutralized with calcium carbonate before determining the aldehyde.—*Yield of formic aldehyde, 0.84 per cent.*

Ethyl Oxide.—(Absolute ether distilled from sodium, boiling between 35° and 36°.) 258 grams gave 4.78 grams formic aldehyde and 12.24 grams acetaldehyde.—*Yield of formic aldehyde, 1.86 per cent.*

Amylene.—(Mainly trimethylethylene. Boiling-point 37° to 40°.) 100 grams gave 2.01 grams formic aldehyde, but no acetic aldehyde. No bath was used.—*Yield of formic aldehyde, 2.01 per cent.*

Normal Propyl Alcohol.—(Boiling-point 96° to 99°.) 56 grams with the bath at 45° to 50° gave 1.53 grams formic aldehyde, but no acetaldehyde.—*Yield of formic aldehyde, 2.72 per cent.*

Trimethylcarbinol.—(Boiling-point 82° to 85°.) 39 grams gave 2.01 grams formic aldehyde, but no acetaldehyde. Temperature of bath, 35° to 40°. The quantity of carbon dioxide formed in the experiment was unusually large.—*Yield of formic aldehyde, 5.17 per cent.*

An oxidation of 150 grams of benzene, free from thiophene, with the bath at 45° to 50°, did not give formic aldehyde in determinable quantity. The oxidation of an equal weight of toluene gave very appreciable quantities of formic aldehyde, but quantitative determinations were not attempted, as it was found that benzoic aldehyde, which was also present, would prevent the successful employment of the Trillat method.

In comparing the yields of formic aldehyde obtained in these experiments, it must be remembered that the values recorded hold true for a single set of conditions only, and that these cannot always have been the most favorable ones possible. The important fact demonstrated is the marked tendency to the production of measurable quantities of formic aldehyde in the partial combustion of numerous carbon compounds belonging to very dissimilar types. So far as yet appears, this reaction is even of more frequent occurrence in such oxidations by air and copper oxide as have been described, than is the more familiar formation of oxalic acid in oxidations by nitric acid. Whether formic aldehyde, in small quantities, is also a frequent product of oxidations in the wet way, we have not attempted to determine. That it may be formed in many reactions of this class is, however, not in the least improbable.

BOSTON, November 26, 1900.

XXIX.—ON THE NON-EXISTENCE OF TRIVALENT CARBON.

BY JAMES F. NORRIS.

In a paper which has recently appeared Gomberg[1] has reported the results of the study of the action of zinc on triphenylchlormethane. It was found that when a solution of the halogen compound in benzene was treated with zinc, a reaction took place slowly at ordinary temperatures and, if air was excluded, at the end of five or six days the chlorine was converted quantitatively into zinc chloride. There remained in solution a highly unsaturated substance which united with iodine at 0°, and was converted into an insoluble oxygen compound when brought into contact with the air. These reactions showed that the compound was not hexaphenylethane, the substance which would be expected as the result of the action of zinc on triphenylchlormethane. The author concluded that the properties of the unsaturated body could only be explained by assuming that it was a free radical. The reaction was expressed by the following equation :

---

[1] J. Am. Chem. Soc., **22**, 757.

$$2(C_6H_5)_3CCl + Zn = 2(C_6H_5)_3C— + ZnCl_2.$$

Analyses and molecular weight determinations of the compound formed by the action of oxygen on the radical gave results which agreed with the formula

$$(C_6H_5)_3C—O—O—C(C_6H_5)_3.$$

As the result of the action of iodine on the radical, triphenyliodomethane was obtained.

In an attempt to prepare tetraphenylmethane in this laboratory by the action of sodium on a mixture of triphenylchlormethane and brombenzene, a preliminary account of which has already appeared,[1] it was found that an oxygen compound was one of the products of the reaction. In seeking the cause of the formation of an oxygen compound from substances containing no oxygen, we were led to study the action of sodium on triphenylchlormethane alone. As the explanation of the reaction which appeared probable to us was quite different from that proposed by Gomberg, and as it did not involve the assumption of a trivalent carbon atom, it seemed important to test the theory by studying the reaction described by Gomberg. As a result, facts have been discovered which furnish an adequate explanation of the reaction without the necessity of introducing any new principles.

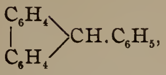
It seemed probable that when zinc reacted with triphenylchlormethane, the metal caused the elimination of hydrogen chloride and not of chlorine alone. This common action of zinc on halogen compounds is shown in the case of the compounds $C_6H_5CH_2Cl$ and $(C_6H_5)_2CHCl$. In the case of triphenylchlormethane the elimination of hydrogen chloride would involve the removal of a hydrogen atom from a benzene ring and not from the methane carbon, as is the case with the two compounds cited. Such a loss of hydrogen chloride has already been observed. Hemilian[2] showed that when triphenylchlormethane was heated to 200°, hydrogen chloride was split off, and among the products formed was a hydrocarbon to which he assigned the formula $(C_6H_5)_2C : C_6H_4$. E. and O. Fischer[3] showed later that the substance had the formula

---

[1] This JOURNAL, 25, 54.

[2] Ber. d. chem. Ges., 7, 1208.

[3] Ann. Chem. (Liebig), 194, 256.



$$\left.\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\right> CH.C_6H_5,$$

by preparing it by the condensation of fluorene alcohol and benzene. Hanriot[1] has assigned the formula $(C_6H_5)_2C : C_6H_4$ to a hydrocarbon formed by the action of potassium on triphenylmethane at 300°. This hydrocarbon is probably identical with the one prepared by Hemilian, as it resembles it closely and does not show the reactions of an unsaturated compound. It is possible that in both cases a substance having the structure suggested by Hemilian was first formed, and that this at the high temperature suffered a molecular rearrangement into the fluorene derivative.

The properties and reactions of triphenylchlormethane are being studied in this laboratory by Mr. Erik Green, who has shown that the compound readily loses hydrogen chloride. When it is treated with concentrated sulphuric acid it goes into solution without rise in temperature, and hydrogen chloride is evolved in large quantities.

When zinc acts upon triphenylchlormethane dissolved in benzene there is no evolution of hydrogen and zinc chloride is formed. This fact does not speak against the theory that the metal removes hydrogen chloride, for the nascent hydrogen formed by the action of the acid on the zinc, as it is produced very slowly during five days, might add itself completely to either a part of the unsaturated compound produced by the reaction or to the benzene used as a solvent. An experiment described below seems to indicate that the latter view is probably correct.

As ethyl acetate is known to have a marked effect on the removal of halogens from their compounds by means of metals, the action of zinc on triphenylchlormethane dissolved in this solvent was studied. It was found that the reaction started in a few seconds and was complete in two to three minutes. In this case, if air was excluded, a solution was obtained in which a white precipitate was formed when it was brought into contact with the air. This precipitate was shown to be identical with the peroxide obtained when the solvent was benzene. When crystallized from carbon disulphide the characteristic hexagonal plates, which have a high index of refraction, were obtained. The reaction was evidently the same as that in benzene solution with the exception that in ethyl acetate the reaction was complete in a few minutes, whereas in benzene, five to six days were required. Further, when ethyl acetate was the solvent, hydrogen was evolved and hydrochloric acid was formed in the solution. An experiment was carried out in the following manner: To about 1 gram of pure, colorless triphenylchlormethane, dissolved in 5 cc. of ethyl acetate, which had been previously shaken with sodium carbonate to remove free acetic acid, was added about 1 gram of powdered zinc. In a short time the solution assumed a pale-yellow color and a gas was given off, which was shown to be hydrogen. As the reaction proceeded the yellow color of the solution increased in depth until it approximated that of a dilute solution of potassium chromate. When the reaction was complete the solution was shaken in contact with the air. A white precipitate was formed and the solution lost its yellow color. The ethyl acetate was found to be acid and to contain zinc chloride. It was shown that zinc has no action upon ethyl acetate under the conditions used in this experiment.

---

[1] Bull. Soc. Chim. [3], 1, 775.

In this experiment the white precipitate, which was shown to be identical with that formed from a benzene solution of the unsaturated compound, was produced by the action of the air on a substance which was formed as the result of the elimination of hydrogen chloride from triphenylchlormethane. It follows, therefore, that in a benzene solution the same reaction takes place. The following equation appears to represent the facts:

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_2C : C_6H_4 + ZnCl_2 + H_2.$$

When ethyl acetate is the solvent less than one-fourth of the theoretical amount of hydrogen is set free, the remainder stays in solution as hydrochloric acid.

When benzene is the solvent the hydrogen is probably added to the benzene, for no triphenylmethane was found in solution after the peroxide was filtered off. The following experiment appears to furnish evidence in favor of this view.

Sodium was added to ether which contained a small quantity of water, and the amount of hydrogen evolved was noted. Some benzene was now added. The evolution of gas was reduced to the extent of almost one-half. The experiment was repeated, using naphthalene instead of benzene. The same result was observed. It has been shown by Bamberger that when naphthalene is added to alcohol containing sodium it is reduced. In the experiment just described it is probable that the naphthalene and the benzene united with a part of the evolved hydrogen.[1]

Gomberg has shown that the structure of the oxide formed by the action of oxygen on the unsaturated compound is best expressed by the formula

$$(C_6H_5)_3C—O—O—C(C_6H_5)_3.$$

A body with this structure could not be produced by the action of oxygen alone on diphenylphenylenemethane,

$$(C_6H_5)_2C : C_6H_4.$$

It might result, however, by the combined action of water and oxygen, or by the action of hydrogen peroxide. An experiment made to test this point showed that the unsaturated hydrocarbon does not unite with dry oxygen. A stream of dry air was drawn through a benzene solution of the compound for twenty minutes and no precipitate was formed. When the solution was exposed to the air the oxide began to separate in a few seconds. When an ethereal solution of hydrogen peroxide and a solution of the unsaturated hydrocarbon in ethyl acetate were mixed, care being taken to avoid the presence of air, a precipitate was slowly formed. The formulas given for the hydrocarbon and the oxide are, therefore, an expression of these facts.

By the action of iodine on the unsaturated compound, Gomberg obtained triphenyliodomethane. The formation of this compound from a substance of the structure $(C_6H_5)_2C : C_6H_4$ could be brought about only by the addition of hydrogen iodide. Even at 0°, in addition to direct addition, substitution with the consequent formation of hydrogen iodide would be expected when such a highly unsaturated compound is treated with iodine. Iodine readily substitutes in compounds which unite with hydrogen iodide. Aniline forms an iodo derivative and methylamine is converted in part into methylamine hydroiodide when it is treated with iodine at 0°.

---

[1] As the benzene used contained thiophene the hydrogen may have been absorbed by it.

All of the reactions of the substance formed by the action of zinc on triphenylchlormethane are easily explained if the compound so formed is diphenylphenylenemethane,

$$(C_6H_5)_2C : C_6H_4.$$

It is of interest to mention the fact that tetrahydronaphthalene resembles diphenylphenylenemethane in some of its properties. It is reduced with difficulty, it absorbs oxygen from the air, and unites with the halogens at low temperatures, halogen hydrides being formed at the same time.

If the structure here proposed is correct, the compound is of unusual interest, as it contains a carbon atom which is linked to two carbon atoms in a single benzene ring. This structure is put forward tentatively. It is an expression of the reactions of the compounds as far as they have been studied, but further work is necessary before it can be accepted. The double-linking between the methane carbon and the benzene ring may resemble that between the carbon and nitrogen atoms in the triphenylmethane dyes. The fact that the compound is colored, indicates that it may have such a quinoid structure. This view will be tested by studying the action of metals on trinitrotriphenylchlormethane, in which the three places in the benzene rings para to the methane carbon, are occupied by nitro groups. The compound may have double the molecular weight of the formula given, in which case it would have a structure somewhat like the accepted quinone structure.

As ethyl acetate has been found to have such a marked influence on the action of zinc on triphenylchlormethane, the action of metals on other halogen compounds dissolved in ethyl acetate will be investigated in this laboratory.

BOSTON, MASS., December 6, 1900.

THE CONSTITUTION OF BENZENE.

BY GEORGE M. RICHARDSON.

The work of Baeyer[1] upon the constitution of benzene has shown that Ladenburg's prism formula for benzene is extremely improbable; but this work did not enable Baeyer to decide definitely for or against either the Kekulé or Claus formula.

The Kekulé formula, showing as it does the occurrence of the ethylene condition three times in the benzene nucleus, is in many respects unsatisfactory, for benzene does not show the properties that we are accustomed to ascribe to the ethylene condition, either in its conduct towards the halogen acids or its behavior towards oxidizing agents.

Claus,[2] in order to avoid Ladenburg's objection to his formula that the ortho and para positions are identical, found it necessary to assume that the para bond is essentially unlike the ortho bond. In so doing, Claus necessarily introduced geometrical conceptions in regard to the molecule, ideas which at that time were not favorably received.[3]

Now that geometrical conceptions are continually being taken into account in the consideration of the structure of carbon compounds, Claus' assumptions do not seem so forced as they once did.

Baeyer has shown then when two hydrogen atoms are added to terephthalic acid they take the para position with regard to one another, as is indicated by the Claus formula.

When two hydrogen atoms are added to dihydroterephthalic acid, they do not go para to one another, but go to the ortho position, showing that in dihydroterephthalic acid there are no para bonds, but instead double linking. This caused Claus[4] to further modify his views by assuming that when the first para bond is broken the two remaining para bonds rearrange themselves to double linking.

---

[1] Ann. Chem. (Liebig) **245**, 103; **251**, 257; **256**, 1; **258**, 1; **258**, 145: **266**, 169; **269**, 145; **276**, 255. This work of Baeyer's is well summarized in his address on the occasion of the Kekulé celebration, Ber. d. chem. Ges., **23**, 1277 (1890).

[2] Ber. d. chem. Ges., **15**, 1405.

[3] See Richard Meyer: Ber. d. chem. Ges., **15**, 1826.

[4] J. prakt. Chem., **145**, 455 (1888).

In ethylene compounds, it is not an uncommon experience to find that the ethylene condition has shifted its position in the course of a chemical reaction. Certain work with muconic acid convinced Baeyer[1] that, even were the Kekulé formula true, in the course of the reduction the position of the double linking would be so readjusted that the first pair of hydrogen atoms added to terephthalic acid would take the para position instead of the ortho position.

The impossibility of getting positive evidence in favor of either Kekulé's formula or Claus' formula, and the lack of entire satisfaction with either of these formulas, led Baeyer[2] to advance the "Centric formula" shortly before suggested by Armstrong.[3] This is a modified Claus formula in which the fourth valence of each carbon atom is supposed to be directed toward the center of the system, but instead of being in combination with the corresponding valence of the para carbon atoms, it is in some unknown manner held in a state of stable equilibrium by the other five similar valences without being necessarily in combination with any one of them.

When a pair of these bonds is removed, as by the addition of two hydrogen atoms, the equilibrium is destroyed and the remaining bonds readjust themselves in some new manner.

By its very nature, this suggestion is incapable of experimental proof. It has, however, the distinct advantage of being a peculiar kind of formula for a peculiar kind of condition, and of being vague just where actual knowledge is vague, and therefore under the present conditions of our knowledge, is perhaps the most satisfactory formula for benzene.

It has seemed to the writer, however, that one feature of the Claus formula, which is lost by merging it into the centric formula, is worth preserving, since it is in accord with a large number of facts. The feature referred to is the expression of a relationship between ortho and para compounds, since these compounds stand together in many chemical reactions as distinguished from meta compounds. It is the purpose of this paper to call attention to this class of phenomena in greater detail than has before been done, and thereby to raise the question, whether, all things considered, the Claus formula does not better represent the structure of benzene than any other formula yet advanced.

---

[1] Ann. Chem. (Liebig) **256**, 1. See also Baeyer's address at the Kekulé celebration, Ber. d. chem. Ges., **23**, 1277.

[2] Ann. Chem. (Liebig), **245**, 127.

[3] J. Chem. Soc., **51**, 263 (1887).

The phenomena to be considered will be taken up under the four heads: *I. The Phenomena of Substitution; II. The Effect of Position of the Substituting Groups upon the Properties of a Compound; III. The Phenomena of Reduction;* and *IV. The Phenomena of Oxidation.*

I. *The Phenomena of Substitution in the Benzene Nucleus.*[1]

When reagents, which are capable of replacing the hydrogen of the benzene nucleus, act upon monosubstitution products of benzene to form disubstitution products, the position assumed by the entering element or group is governed by the character of the group already present in the monosubstitution product.

If the group already present is a halogen element, or has a basic character, such as Cl, Br, I, CH_3, CH_2Cl, $CHCl_2$, CCl_3, OH, NH_2, NHAc, NH_2HCl, CH_2COOH, CHCHCOOH, the new element or group entering takes the ortho- or para-position. Usually both ortho and para compounds are formed simultaneously, sometimes one in excess and sometimes the other, the proportions between the two being frequently more or less controlled by the conditions of the experiment.

On the other hand, if the group present in the monosubstitution product has an acid character (the halogen elements being excepted), such as: NO_2, CN, COOH, CHO, $COCH_3$, $COCH_2Br$, COC_6H_5, SO_2OH, $SO_2C_6H_5$, the second entering group takes the meta-position.

From this it would seem that the ortho and para positions have something in common which distinguishes them from the meta position. This relation is expressed better by the Claus formula than by any of the other benzene formulas now in use.

From this formula (Fig. I.), it will be seen that carbon atom 1 is in direct combination with carbon atoms 2, 6, and

---

[1] Armstrong (J. Chem. Soc., **51**, 258, 579, and 583) has considered the laws of substitution and their bearing on the structure of benzene, but the conclusions reached differ materially from those developed here.

4, while with carbon atoms 3 and 5, it is not in direct combination. Ladenburg's prism formula (Fig. II.), or the modified prism or star formula (Fig. III.), indicating as they do, a direct combination between carbon atoms 1 and 3, 1 and 5, 1 and 4, and hence, a similarity between meta and para compounds as distinguished from the ortho compounds, is not so well in accord with the facts.

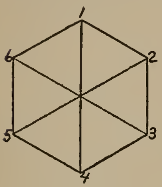


Fig. I.

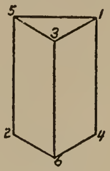


Fig. II.

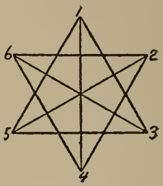


Fig. III.

Now if position 1 in the Claus formula is occupied by a basic group, the action of acid reagents upon that carbon atom will be increased, but in this case there is no more hydrogen attached to carbon atom 1 to be replaced, so the acid reagents act upon those carbon atoms most intimately related to carbon atom 1, that is, upon those in direct combination with it, and replaces the hydrogen atoms attached to carbon atoms 2, 6, or 4, to form ortho and para compounds.

If, however, position 1 is occupied by an acid group (chlorine, bromine, and iodine being excepted, since these cause the formation of ortho and para compounds) it would render carbon atom 1 less susceptible to the action of acid reagents, and this influence would extend to the carbon atoms immediately connected with carbon atom 1; that is, to carbon atoms 2, 6, and 4. Carbon atoms 3 and 5 would therefore of the whole molecule be the atoms most likely to be attacked by the acid reagent; that is, meta compounds would be formed.

If these suggestions as to the cause of the phenomena observed are correct, it seems probable that if the second entering group were of a basic character, or of such a character as to be attracted by acid groups already present in the monosubstitution product, acid groups would cause the formation of ortho and para compounds instead of meta compounds, and basic groups would cause the formation of meta compounds instead of ortho and para compounds. This point cannot at present be experimentally tested, as we do not know any basic group that can be substituted for the hydrogen of benzene by direct action of a substituting agent. The formation of resorcin by fusing with caustic potash at high temperatures both the ortho- and parabrombenzenesulphonic acid, as well as the corresponding meta compound, and the preponderance of metaxylene in coal-tar are phenomena that may be due to this cause.

In a general way we think of an acid group and a basic group as having an attraction for one another, and think of two groups of the same kind, two acid groups or two basic groups as having little or no attraction for one another, or even as having a repulsion for one another. Doubtless in the main such assumptions are correct, but that such is uniformly the case cannot safely be assumed.

Our knowledge of the preference which organic groups have for each other, or for other elements is very imperfect.

This point has been considered in the discussion on the "most favorable configuration" of organic molecules containing two singly linked asymmetric carbon atoms, and the lack of exact information is well illustrated by the lack of unanimity in the opinion of the most prominent workers in this field. Wislicenus assumes that methyl groups do not attract one another, but that they repel one another. Bischoff assumes that the repulsion is very weak between the methyl groups, while Baeyer assumes that methyl groups attract one another. Bischoff has assumed a repulsion between methyl and carboxyl, while other writers have assumed that these groups attract each other.

It is nevertheless rather surprising to find the halogen elements acting with the basic groups, and according to the views here expressed, attracting other halogen elements and acid groups, causing the formation of ortho and para compounds instead of meta compounds. But that they are attractive to other halogen elements, and to acid groups when combined with carbon, seems to be true, judging from their behavior in the paraffin series.

When hydrochloric acid is added to an unsaturated ethylene hydrocarbon, the chlorine goes to the carbon atom which is combined with the least hydrogen ; *e.g.*, $CH_2CH\ CH_3$ gives $CH_3CHClCH_3$, and not $CH_2ClCH_2CH_3$.

When the two unsaturated carbon atoms hold the same amount of hydrogen, the chlorine goes to that carbon atom holding the simplest radical ; *e.g.*, $CH_3CHCHCH_2CH_3$ gives $CH_3CHClCH_2CH_2CH_3$, and not $CH_3CH_2CHClCH_2CH_3$, in this case illustrating the greater affinity of chlorine for methyl than for ethyl. A corresponding phenomenon in the benzene series is seen when the halogens act upon cymene or para-ethyl toluene; the halogen element always assumes a position ortho to the methyl, and meta to the more complex radical.

In the ethylene series if one of the unsaturated carbon atoms is attached to chlorine, the second chlorine atom will go to the same carbon atom ; *e. g.*, CH_2CHCl gives with hydrochloric acid, CH_3CHCl_2, and not CH_2ClCH_2Cl, thus illustrating the power of chlorine to attract chlorine.

Other acid groups appear to repel the chlorine ; *e. g.*, $CH_2CHCOOH$ gives CH_2ClCH_2COOH and not CH_3CHCl $COOH$; this fact is frequently utilized in the preparation of β-chlor acids, and is parallel to the formation of meta-compounds in the benzene series under similar conditions.

In chlorinating saturated hydrocarbons, the first chlorine atom will go to the carbon atom in combination with the least hydrogen ; if, however, one chlorine atom is already in the compound, the second chlorine atom wherever possible will go to the same carbon atom, or to the carbon atom immediately adjoining.

As is well known, it is more difficult to chlorinate acetic acid than it is to chlorinate marsh gas, the difference being due presumably to the lack of affinity between the chlorine and the carboxyl group. Acetyl chloride is, however, easier to chlorinate than acetic acid, illustrating again the favorable action of chlorine already present in a compound upon the chlorination process.

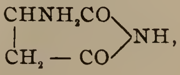
The direct chlorination of propionic acid gives α-chlor-propionic acid. Here the tendency of the chlorine atom to go to the carbon atom which is in combination with the least hydrogen (due perhaps to the attractive power of the methyl group which is in combination with that carbon atom), is greater than the retarding influence of the carboxyl group. With normal butyric acid, $CH_3CH_2CH_2COOH$, direct chlorination gives β-chlorbutyric acid, $CH_3CHClCH_2COOH$, both the carboxyl and the methyl groups tend to cause the chlorine to take this position.

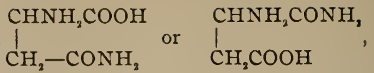
If, however, butyryl chloride, $CH_3CH_2CH_2COCl$, is chlorinated, α-chlorbutyryl chloride, $CH_3CH_2CHClCOCl$, is obtained, again illustrating the power of chlorine to attract chlorine.

With chlorine and hydrochloric acid, the tendencies here mentioned are so strong, that isomeric modifications are seldom formed. With bromine and hydrobromic acid, with iodine and hydriodic acid, the same tendencies are observed, but in a less marked degree; so that as a rule isomeric modifications are formed; *e. g.*, CH_3CHCH_2 gives with hydrobromic acid both $CH_3CHBrCH_3$ and $CH_3CH_2CH_2Br$, but the former is the chief product of the reaction. Parallel to this we find in the benzene series that the chlorination of benzoic acid gives only metachlorbenzoic acid, while the bromination of benzoic acid gives chiefly metabrombenzoic acid, but also gives some orthobrombenzoic acid.

The fact that the acid chlorides are easier to chlorinate than the free acids, and that they tend to form α-chlorderivatives, suggests the possibility that in the chlorination of benzoyl chloride, some ortho chlorbenzoyl chloride might be formed, and in the bromination of benzoyl bromide the yield of the ortho compound might be increased. Too little is known with regard to the substituting action of other agents than the halogens in the paraffin series to give any general rules.

The addition of water to the imides of the substituted dibasic acids might give some evidence on the point of attraction and repulsion between various organic radicals.

The imide of aspartic acid, for example,  $\left.\begin{array}{l} CHNH_2CO \\ | \\ CH_2 - CO \end{array}\right\rangle NH$, takes up water to form



$$\begin{array}{l}\mathrm{CHNH_2COOH} \\ | \\ \mathrm{CH_2{-}CONH_2}\end{array} \quad \text{or} \quad \begin{array}{l}\mathrm{CHNH_2CONH_2} \\ | \\ \mathrm{CH_2COOH}\end{array},$$

or both. In this particular case it is believed that the former compound is formed rather than the latter. An inspection of the formula with a consideration of the probable attractions and repulsions would indicate that the carboxyl group would go to the carbon holding the amido group, or that the two amido groups, other things being equal, would tend to be as far apart as possible.

Too few examples of this kind of action have yet been examined to permit of any conclusions being based upon them.

So far as our present experience goes, the facts appear to be in accordance with the following generalization:

If the group present in the benzene nucleus attracts the entering group, it will form ortho and para compounds. If, on the other hand, it repels the entering group, meta compounds will be formed. When the attraction or repulsion between the groups is not marked, all three classes of compounds may be formed simultaneously.

II. The Effect of the Position of the Substituting Groups upon the Properties of the Compound.

Halogen elements held in the benzene nucleus are not usually replaced by the amido group by the action of ammonia, or replaced by hydroxyl, by the action of potassium hydroxide.

If, however, the halogen element has a nitro group, ortho or para to it, it may then be replaced by the amido group by the action of ammonia, or by the hydroxyl group by the action of potassium hydroxide. If the nitro group is in the meta position with regard to the halogen element, it has much less influence upon the halogen element, for such a halogen element is not acted upon by ammonia or caustic potash. A nitro group attached to a carbon atom weakens the hold of other electronegative atoms upon that carbon atom. This kind of influence may even extend to the carbon atoms immediately connected with the carbon atom holding the nitro group.[1] Hence, in the Claus formula, if a nitro group is in the position, 2, 6, or 4, it would weaken the hold of the chlorine upon carbon atom 1. A nitro group attached to carbon atom 3 or 5 (that is in the meta position), since these carbon atoms are not in direct combination with carbon atom 1, would have much less action upon the chlorine attached to carbon atom 1.

The fact that one group exerts a stronger influence over another when in the ortho- or para-position with regard to it, than when in the meta-position with regard to it, may be farther illustrated.

The presence of a nitro group in a compound tends to increase its acid properties, or to decrease its basic properties, as for example, the nitrophenols are much stronger acids than phenol itself, and the nitroanilines are much weaker bases than aniline. Ortho- and para-nitrophenol are strong acids, much stronger than the metanitrophenol, which is only a slightly stronger acid than phenol.

From an examination of the possible formulas for the trinitrophenols, we should choose that of picric acid, $C_6H_2OHNO_2NO_2NO_2$ (1, 2, 4, 6,), as the one representing the strongest acid properties, and this appears to be in accordance with the facts.

Of the three nitranilines, ortho- and para-nitraniline are very weak bases, their salts being decomposed by water.

Meta-nitraniline is a much stronger base; it salts may be crystallized from water without decomposition.

Ortho-nitrobenzoic acid is the strongest of the three nitrobenzoic acids.

In so far as the data of this class are considered, it is practically impossible to decide between the ortho- and para-positions, as to which of these is the position of greatest influence, for in some cases it seems to be one, and in some cases the other. Also with the substitution products, sometimes it is the ortho compound that is formed in the greater quantity, and sometimes it is the para compound. If the Claus formula were to be accepted as correct, even then it would be very difficult to say which would have the greater influence. It must be assumed that the para bond of the Claus formula is weaker than the ortho bond, since it is always the para bond that is broken in the formation of addition products. It might well be that the same cause which weakens the para bond would also tend to weaken the influence of a group in the para position as compared with its influence in the ortho position. However, this may be, we now come to consider a class of phenomena, where, with very few exceptions, groups in the ortho position are seen to have a greater influence than when in the para position, and groups in the para position have a greater influence than when in the meta position.

---

[1] That groups which are attached to a carbon atom may have an influence upon the affinity of carbon atoms immediately adjoining, is frequently assumed. As an example, we may take the assumption made with regard to chloral hydrate, the formula of which is written, $CCl_3CH(OH)_2$. Here the unusual power which enables one carbon atom to hold in combination two hydroxyl groups is attributed to the influence of the three chlorine atoms which are in combination with the neighboring carbon atom.

III. The Phenomena of Reduction.

If we were to draw any conclusions in regard to the processes of reduction from the conceptions advanced here, they would be as follows: The presence of a substituting group in a benzene compound which also contained a reducible group, as for example, nitrobenzene would increase the ease of reduction of the nitro-group if the substituting group were of a character to attract the reducing agent, and would increase the difficulty of reduction if the substituting group were of such a character as to repel the reducing agent. Moreover, the substituting group would presumably produce its maximum effect when ortho to the reducible group, a somewhat less but similar effect when para to the reducible group, and a much less effect, or perhaps no appreciable effect at all, when in the meta-position with regard to the reducible group.

In a general way we think of basic groups as being attractive to acid reducing agents, and non-attractive to alkaline reducing agents; and of acid groups as being attractive to alkaline reducing agents and non-attractive to acid reducing agents. That there may be exceptions to this classification is quite probable. We have already seen that the acid halogen elements, when combined with carbon appear to have an attraction for other halogen elements and for acid groups.

There is a large amount of data scattered through the chemical literature in regard to the reduction of benzene compounds, but so far as I can learn it has never been brought together and few generalizations have been made in regard to it. I shall present here some of the facts in regard to the reduction of nitro compounds with tin and hydrochloric acid; with stannous chloride and hydrochloric acid; with hydrogen sulphide in ammonia solution; and with ammonia itself in aqueous or alcoholic solution.[1]

It may be said at once that the results thus far brought together confirm in a most striking manner the generalizations made above.

Tin and hydrochloric acid[2] will reduce all of the nitro groups present in a compound, and in all situations.

No group acid or basic is capable of protecting a nitro group from reduction by these reagents. The same is true of stannous chloride and hydrochloric acid. When a compound contains two or more nitro groups the nitro groups may be reduced one at a time by using the proper amounts of tin or of stannous chloride (the latter is more satisfactory for partial reductions in actual practice). By noting the order in which the nitro groups are selected for reduction by the reducing agent, we can get evidence on the points in question. As to the order of selection tin and stannous chloride in hydrochloric acid behave precisely alike, as would be expected.

When di- and trinitrobenzene compounds are reduced by hydrogen sulphide in ammonia solution only one nitro group is reduced at first, a second nitro group may or may not be reduced by this reagent, depending upon the nature of the other groups present. The reduction of the second group is favored by the accumulation of negative groups in the compound, especially if in the ortho or para position with reference to the nitro group to be reduced. It is hindered or altogether prevented by basic groups ortho or para to the nitro group. The protective power of an amido group ortho to a nitro group is especially marked so far as this reducing agent is concerned.

---

[1] Most of the facts here given have been collected for me by Mr. W. D. Harkins.

[2] Ber. d. chem. Ges., **11**, 35 and 40; **20**, 1567; **19**, 2161.

Ammonia in aqueous or alcoholic solution is frequently used to convert the nitro group into the amido group. It is probable that this is not a true reduction but rather an exchange of the nitro group for the amido group, according to the equation:

$$C_6H_4NO_2NO_2 + NH_3 = C_6H_4NO_2NH_2 + HNO_2 \text{ or}$$
$$C_6H_4NO_2NO_2 + 2NH_3 =$$
$$C_6H_4NO_2NH_2 + (NH_4NO_2) = 2H_2O + 2N.$$

It is known for example that, if the nitro group is ortho or para to chlorine, it is the chlorine and not the nitro group that is replaced by the amido group. Whether the reaction be a true reduction or merely an exchange of the nitro group for an amido group, the evidence furnished upon the points in question is the same.

(1) *Influence of Methyl Group upon the Reduction of the Nitro Group.*

Beilstein and Kuhlberg[1] have shown that dinitrotoluene, $C_6H_3CH_3NO_2NO_2$ (1, 2, 4), when reduced with ammonium sulphide, gives nitroparatoluidine, $C_6H_3CH_3NO_2NH_2$ (1, 2, 4).

Anschütz and Heusler[2] have shown that the same dinitrotoluene, $C_6H_3CH_3NO_2NO_2$ (1, 2, 4), when reduced with stannous chloride and hydrochloric acid, gives nitro orthotoluidine, $C_6H_3CH_3NH_2NO_2$ (1, 2, 4) without a trace of the isomer formed when ammonium sulphide is used as a reducing agent.

Cunerth[3] states that the dinitrotoluene, $C_6H_3CH_3NO_2NO_2$ (1, 2, 5), when reduced with ammonium sulphide, gives the nitrometatoluidine, $C_6H_3CH_3NO_2NH_2$ (1, 2, 5).

Tiemann[4] has shown that trinitrotoluene, $C_6H_2CH_3NO_2NO_2NO_2$ (1, 2, 4, 6), when reduced with ammonium sulphide, gives dinitroparatoluidine, $C_6H_2CH_3NO_2NH_2NO_2$ (1, 2, 4, 6), and the trinitro toluene, $C_6H_2CH_3NO_2NO_2NO_2$ (1, 3, 4, 6), gives with alcoholic ammonia dinitrometatoluidine, $C_6H_2CH_3NH_2NO_2NO_2$ (1, 3, 4, 6).

---

[1] Ann. Chem. (Liebig), 155, 14.

[2] Ber. d. chem. Ges. 19, 2161.

[3] Ann. Chem. (Liebig), 172, 223.

[4] Ber. d. chem. Ges., 3, 218.

Grevingk[1] finds that dinitrometaxylene, $C_6H_2CH_3NO_2CH_3NO_2$ (1, 2, 3, 4), when reduced with ammonium sulphide, gives the nitroxylidine, $C_6H_2CH_3NO_2CH_3NH_2$ (1, 2, 3, 4).

Fittig[2] states that the dinitroparaxylene, $C_6H_2CH_3NO_2CH_3NO_2$ (1, 2, 4, 5,), when reduced with ammonium sulphide, gives the nitroxylidine, $C_6H_2CH_3NH_2CH_3NO_2$ (1, 2, 4, 5), and the dinitroparaxylidine, $C_6H_2CH_3NO_2CH_3NO_2$ (1, 2, 4, 6), when reduced with ammonium sulphide, gives the nitroxylidine, $C_6H_2CH_3NH_2CH_3NO_2$ (1, 2, 4, 6), but that the former of these, is reduced much more easily than the latter. In both these cases the nitro groups are ortho to one methyl group and para to the other, so that the methyl groups would not effect the comparative ease of reductions of the two compounds. It seems therefore, that the difference must be due to the different relations of the two nitro groups to each other in the two compounds, and we should infer that the nitro group must aid reduction with ammonium sulphide more when in the para position than when in the meta position.

In every case which has come under my notice the methyl group seems to have the effect predicted for it upon reducing agents.

(2). *Influence of Chlorine upon the Reduction of Nitro Groups.*

Beilstein[3] states that orthochlornitrobenzene is not reduced by ammonium sulphide, while the para- and metachlornitrobenzene are reduced.

Claus and Stiebel[4] found that the chlordinitrobenzene, $C_6H_3ClNO_2NO_2$ (1, 2, 4), when reduced with stannous chloride and hydrochloric acid, gave as the chief product the chlornitraniline, $C_6H_3ClNH_2NO_2$ (1, 2, 4); but at the same time a small amount of the isomeric chlornitraniline, $C_6H_3ClNO_2NH_2$ (1, 2, 4), was formed.

Laubenheimer[5] states that the chlordinitrobenzene, $C_6H_3ClNO_2NO_2$ (1, 3, 4), when heated with ammonia, gives the chlornitraniline, $C_6H_3ClNH_2NO_2$ (1, 3, 4). Here the fact that one nitro group is replaced by an amido group is doubtless due to the favorable action of the second nitro group ortho to the nitro group replaced, for the metachlornitrobenzene, $C_6H_4ClNO_2$ (1, 3), is not acted upon by ammonia. But the chlorine apparently exerts a sufficient retarding influence upon the action of the ammonia to cause the nitro group meta to the chlorine to be selected rather than the nitro group para to the chlorine.

---

[1] Ber. d. chem. Ges., **17**, 2425.

[2] Ann. Chem. (Liebig), **147**, 18 and 22.

[3] Ber. d. chem. Ges., **11**, 2056.

[4] Ber. d. chem. Ges., **20**, 1379.

Ber. d. chem. Ges., **9**, 1826.

From all the data found in regard to the action of chlorine upon the reduction of the nitro group, it appears that chlorine ortho to a nitro group favors its reduction with acid reducing agents and retards its reduction with alkaline reducing agents. Hence chlorine acts here with the basic elements as it does in the phenomena of substitution.

(3) *Influence of Hydroxyl Groups upon the Reduction of Nitro Groups.*

Stuckenberg[1] has shown that dinitrophenol, $C_6H_3OHNO_2NO_2$ (1, 2, 4,), when reduced with ammonium sulphide, gives the nitroamidophenol, $C_6H_3OHNH_2NO_2$ (1, 2, 4).

Griess[2] states that the chlordinitrophenol, $C_6H_2OHNO_2NO_2Cl$ (1, 2, 4, 6), when reduced with ammonium sulphide gives the chlornitroamidophenol, $C_6H_2OHNH_2NO_2Cl$ (1, 2, 4, 6).

Picric acid[3] when reduced with ammonium sulphide, or with alkaline solutions of ferrous sulphate, or with an acetic acid solution of ferrous salts has one of the nitro groups, that is ortho to the hydroxyl group reduced. The second ortho nitro group may also be reduced by ammonium sulphide.[4]

Data concerning the partial reduction of the polynitrophenols with acid reducing agents, we have not been able to find with the exception of the partial reduction of picric acid with acetic acid solution of ferrous salts mentioned above.

Finding that hydroxyl acts with the basic groups in the formation of substitution products, according to the views here set forth, we should expect it to favor the action of acid reducing agents. From the data given above, it evidently favors the action of alkaline reducing agents. In hydroxyl, then, we have a group that appears to be attractive to both acid and alkaline reagents.

---

[1] Ann. Chem. (Liebig), **205**, 72.

[2] *Ibid.*, **109**, 291.

[3] Girard: Compt. rend., **36**, 421; **42**, 59. See also Pugh: Ann. Chem. (Liebig), **96**, 83.

[4] Griess: Ann. Chem. (Liebig), **154**, 202.

(4) *Influence of the Sulphonic Acid Group upon the Reduction of the Nitro Group.*

The only case that we have been able to find that would bear on this point, is that of the partial reduction of the dinitrobenzenesulphonic acid, $C_6H_3SO_3HNO_2NO_2$ (1, 2, 4,), mentioned by Nietzki and Helbach,[1] and which gives the nitroamidobenzenesulphonic acid, $C_6H_3SO_2HNO_2NH_2$ (1, 2, 4), but unfortunately the authors do not mention the reducing agent used.

(5) *Influence of the Carboxyl Group upon the Reduction of the Nitro Group.*

Ortho- and paranitrobenzoic acids are much easier to reduce with ammonium sulphide than metanitrobenzoic acid.

Little other evidence on the effect of the carboxyl group has been found, as in those cases where data were found the nitro groups were symmetrically situated with regard to the carboxyl group and so gave no evidence upon the point in question.

The data above given concerning the phenomena of reduction certainly are in accordance with the generalizations here advanced. The writer makes no claim to have made an exhaustive search of the chemical literature for data upon this subject, but it should be said that the data here given have not been *selected* to prove the views advanced. Everything found that has any bearing upon the point has been mentioned.

IV. The Phenomena of Oxidation.

Applying the same line of reasoning to the phenomena of oxidation, as was applied to the phenomena of reduction, the same variations in the action of acid and alkaline oxidizing agents are to be looked for as occur with acid and alkaline reducing agents. That is, acid groups ortho to an oxidizable group will decrease the action of acid oxidizing agents upon the oxidizable group, and increase the action of alkaline oxidizing agents. Basic groups ortho to an oxidizable group would decrease the action of alkaline oxidizing, and increase the action of acid oxidizing, agents upon the oxidizable group.

---

[1] Ber. d. chem. Ges., **29**, 2448.

Groups in the para position would exercise a like but less strong influence, and groups in the meta position would exercise still less influence, and frequently no appreciable influence at all.

These deductions are in close accord with Remsen's law[1] of oxidation which may be stated as follows: The presence of an acid or negative group in the benzene nucleus, ortho to an oxidizable side-chain, protects that side-chain from oxidation with acid oxidizing agents, and apparently[2] renders it more prone to oxidation with alkaline oxidizing agents.

For the vast majority of the cases thus far investigated, this law holds good. The sulphamide group, and the sulphonic acid group have been found in a few cases[3] to act not in accord with this law.[4]

The data obtainable in regard to the action of basic groups, ortho to an oxidizable group, are more meagre since most of the basic groups, such as the NH_2, CH_3, CH_2Cl, etc., themselves suffer change during the process of oxidation.

With regard to the action of the hydroxyl group some data are obtainable.

Jacobsen[4] states that the oxymetaxylene, $C_6H_3CH_3CH_3OH$ (1, 3, 4), when fused with caustic potash gives the oxymetatoluic acid, $C_6H_3CH_3COOHOH$ (1, 3, 4), and that oxyparaxylene, $C_6H_3CH_3OHCH_3$ (1, 3, 4,), under like conditions gives the oxyparatoluic acid, $C_6H_3CH_3OHCOOH$.

Oxymesitylene,[5] $C_6H_2OHCH_3CH_3CH_3$ (1, 2, 4, 6,), upon fusion with caustic potash, gives the acid, $C_6H_2OHCOOH$ CH_3CH_3 (1, 2, 4, 6). From these data, it appears that the hydroxyl group favors the action of alkaline oxidizing agents, and thus corresponds to its action with alkaline reducing agents (see page 136). Unfortunately we have found no data as to the behavior of the hydroxyl group toward acid oxidizing agents. Facts concerning the behavior of the hydroxyl group toward both acid oxidizing agents and acid reducing agents are very much to be desired.

---

[1] This Journal, **4**, 143.

[2] *Ibid.*, 8, 262.

[3] Hall and Remsen: *Ibid.*, **2**, 230; Remsen: *Ibid.*, 8, 263.

[4] Ber. d. chem. Ges., **11**, 375.

[5] Hall and Remsen: This Journal, **2**, 141.

Concerning the Halogen Elements.

Since the halogen elements when combined with carbon appear to attract acid reagents as shown by the phenomena of substitution already mentioned, and since chlorine, as has been pointed out (page 136) favors the action of acid reducing agents and retards the action of alkaline reducing agents, we should expect it to favor the action of acid oxidizing agents and retard the action of alkaline oxidizing agents, and hence, to stand in direct opposition to Remsen's law. These conclusions, however, do not appear to be altogether in accord with the facts.

Beilstein and Vollrath[1] state that chlormetaxylene, $C_6H_3CH_3CH_3Cl$ (1, 3, 4), when oxidized with chromic acid gives the chlortoluic acid, $C_6H_3COOHCH_3Cl$ (1, 3, 4), indicating that chlorine protects the ortho methyl group.

Trichlormetaxylene, $C_6HCH_3ClCH_3ClCl$ (1, 2, 3, 4, 6), according to Vollrath, resists entirely the oxidizing action of chromic acid and of nitric acid, again showing protection to the ortho methyl group by the chlorine.

Schmitz[2] states that bromine in brommesitylene protects the two ortho methyl groups from oxidation with chromic acid.

The same is true of chlorine in chlormesitylene.[3]

Von Gerichten[4] has shown that chlorcymene, $C_6H_3CH_3ClC_3H_7$ (1, 2, 4), when oxidized with chromic acid gives chlortoluic acid, $C_6H_3CH_3ClCOOH$ (1, 2, 4). This action however may well be due to the general tendency of the propyl group of cymene to suffer oxidation before the methyl group, rather than to any protective action of the chlorine. The isomeric chlorcymene, $C_6H_3CH_3ClC_3H_7$ (1, 3, 4), gave by oxidation an acid, $C_6H_3COOHClC_3H_7$, or $C_6H_3CH_3ClC_2H_4COOH$; von Gerichten himself believed it to be the latter; if it were the former acid the protective power of the chlorine would be clearly shown.

---

[1] Ann. Chem. (Liebig), **144**, 266 and 271.

[2] *Ibid.*, **193**, 171; also **147**, 8.

[3] *Ibid.*, **150**, 325.

[4] Ber. d. chem. Ges., **11**, 364 and 1719.

Remsen and Morse[1] find that bromparaethyltoluene, $C_6H_3CH_3BrC_2H_5$ (1, 2, 4), when oxidized with chromic acid, gives bromparatoluic acid, $C_6H_3CH_3BrCOOH$ (1, 2, 4). Here also this may be due to the fact that paraethyltoluene when oxidized gives paratoluic acid and no paraethylbenzoic acid, rather than to any protective influence of the bromine. If the isomeric bromparaethyltoluene, $C_6H_3CH_3BrC_2H_5$ (1, 3, 4), were to give the acid, $C_6H_3COOHBrC_2H_5$ (1, 3, 4), then the protective influence of bromine would be clearly shown.

The facts quoted tend to confirm Remsen's law and to prove false the assumptions made here, nevertheless a few statements have been found that are in accord with these assumptions and apparently in conflict with the facts just quoted.

Fittig[2] states that orthochlortoluene is completely burned up by chromic acid, showing that chlorine intensifies the action of chromic acid.

Noyes[3] has found that both ortho- and parabromtoluene are more difficult to oxidize, than toluene itself with alkaline solution of potassium ferricyanide, and that the ortho compound is more difficult to oxidize than the para compound. Later, Noyes and Walker[4] point out that metabromtoluene is the easiest of the three bromtoluenes to oxidize with alkaline potassium ferricyanide solution,—facts which illustrate the retarding influence of bromine upon alkaline oxidizing agents, and as well the relative influence of the ortho, meta, and para positions according to the assumption here made. Further investigation of the action of the halogen elements toward both acid and alkaline oxidizing agents, and toward acid and alkaline reducing agents are very desirable, in order to learn whether or not these two classes of phenomena show similar variations.

Finally, as regards the actual influence of the meta position, there is much less evidence than for the other positions, but the little evidence obtainable, goes to show that in the meta position, groups have very little influence.

---

[1] This Journal, **1**, 138.

[2] Ztschr. Chem., N. F., **7**, 179.

[3] This Journal, **5**, 105.

[4] *Ibid.*, 8, 186.

Noyes and Moses[1] have shown that metanitrotoluene is much more difficult to oxidize with alkaline potassium ferricyanide than either the ortho- or paranitrotoluene. Upon this point the authors say: "Their conduct seems to indicate that it is not so much that a nitro group in the meta position protects a methyl group, as that a nitro group in the ortho or para position has, as it were, a loosening effect on a methyl group, causing the latter to be more easily attacked by the oxidizing agent which we are studying."

Remsen and Palmer[2] have shown that metatoluenesulphamide is oxidized with equal facility, with both acid and alkaline oxidizing agents.

To repeat, in conclusion, so far as all of the phenomena of the four classes here considered are concerned, it seems to the writer that the Claus formula is better in accord with the actual properties of benzene compounds, than any other benzene formula that has yet been suggested.

Applying the van 't Hoff-LeBel theory to the Claus formula, using tetrahedrons to represent the carbon atoms, we get as the configuration of the benzene molecule,

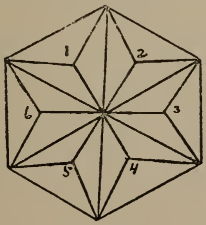


Fig. IV.

or

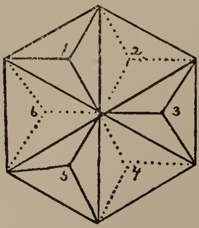


Fig. V.

In the first the apices of the tetrahedrons showing the positions of the hydrogen atoms are all in one plane on the same side of the molecule. In the second the hydrogen atoms lie alternately in two planes, one above and the other below the plane of the carbon atoms. The former of these has been suggested by Loschmidt.[1] Baeyer[2] has also suggested essentially the same configuration in connection with his "centric formula." The second form given above has been suggested by Marsh[3] and by Vaubel.[4]

---

[1] This Journal, 7, 149.

[2] *Ibid.*, 4, 142.

Vaubel's chief reason for preferring his formula to that of Loschmidt, is that in it the ortho and the para positions are on the same side of the molecule, and on the opposite side of the molecule from the meta-position. Hence the ortho- and para-positions have properties in common which distinguish them from the meta position. On this point he says[5]: "This configuration shows us that in the formation of ortho and para-derivatives the substituting groups occupy different sides of the molecule. We can in this case assume that the substituting groups exercise a mutually repelling action. When they attract one another, on the contrary, meta derivatives will be obtained, which may be induced by the action of heat or some similar influence to go over into ortho- and para derivatives."

It will be observed that the assumptions here made are the exact reverse of the conclusions set forth in this article, and it appears to the writer that Vaubel's assumptions in this regard are not warranted when the nature of the groups that assume the different relations with respect to each other is taken into consideration. Moreover, in the Vaubel formula groups which are in the ortho position (*e. g.*, the carboxyl groups in phthalic acid) have the fumaroid relation to one another, which we have learned is characterized by the inability to form an anhydride. But the ortho-compounds in the benzene series are just those which best give anhydrides. It appears, therefore, from this point of view, that the Loschmidt formula in which groups in the ortho position have the maleinoid relation is the preferable one.

Again Baeyer has shown that when terephthalic acid is reduced with sodium amalgam two geometrically isomeric $\Delta^{2.5}$

---

[1] Monatsh. f. Chem., **11**, 28 (1890).

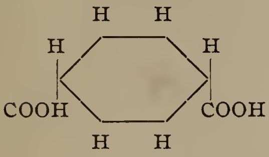
[2] Ann. Chem. (Liebig), **245**, 123.

[3] Phil. Mag., Nov., 1888.

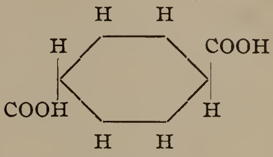
[4] J. prakt. Chem. (2), **44**, 137; **48**, 75, 315; **49**, 308, 540; **50**, 58, 362; **51**, 444; **52**, 417, 548; **53**, 241, 549.

[5] *Ibid.*, **44**, 142.

dihydroterephthalic acids are formed,[1] the maleinoid or cis form and the fumaroid or cistrans form which may be represented by the figures:



Cis form.



Cistrans form.

As the formulas indicate, the cistrans form is, like fumaric acid, the more stable (the carboxyl groups tending to get as far apart as possible), the cis form being changed into the cistrans by heating with hydrochloric acid. Now if the Vaubel formula is correct, simple reduction would give at once the cistrans modification and as this form does not tend to pass over into the cis form we should expect by this simple reduction to get only the cistrans form. The Loschmidt formula would by simple reduction give only the cis modification, but as this tends to pass over into the cistrans modification both modifications would be present in the reduction product unless unusual precautions were taken to prevent the secondary reaction.

Baeyer[1] also concludes that the hexahydromellitic acid obtained by the direct reduction of mellitic acid is the maleinoid form. The Loschmidt formula would account for this, but the Vaubel formula would indicate the formation of the fumaroid hexahydromellitic acid.

In the Loschmidt formula if one of the para bonds is broken the remaining para bonds can rearrange themselves in the form of double bonds with little or no change in the geometrical configuration. Indeed Loschmidt proposed this configuration assuming the three double bonds of the Kekulé formula; that is, he assumed that carbon atoms 1 : 2, 3 : 4, and 5 : 6 in Fig. IV are connected by double bonds and that carbon atoms 2 : 3, 4 : 5, and 5 : 6, are joined by single bonds.

---

[1] Ann. Chem. (Liebig), **251**, 290 and 296.

[1] *Ibid.*, **245**, 134.

This configuration, along with Vaubel's, indicates better than any other configuration the fact that in some cases (as for example with phloroglucin) the three double bonds might be present without essential alteration of the configuration.

If any value whatever can be attached to the suggestions put forth in this paper, it is that they bring together and show an apparent relation between a considerable number of facts which have hitherto been considered as independent phenomena. Their chief merit, however, is the fact that experimental evidence can rapidly be accumulated which will render them much more probable than they now seem; or else will render them wholly untenable.

STANFORD UNIVERSITY, CALIFORNIA,
May 25, 1900.

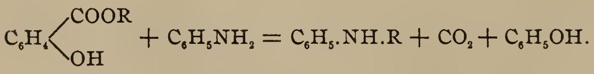
Contributions from the Havemeyer Laboratories of Columbia University.

XXXIX.—THE SYNTHESIS OF AMINES BY THE USE OF ALKYL SALICYLATES.

By ALFRED TINGLE.

THEORETICAL.

It has been previously shown[1] that when alkyl salicylates are boiled with an excess of aniline, the alkyl group is introduced into the aniline molecule, a secondary amine being produced. The reaction may be expressed by the following equation:



$$C_6H_4\begin{matrix}\diagup COOR\\ \diagdown OH\end{matrix} + C_6H_5NH_2 = C_6H_5.NH.R + CO_2 + C_6H_5OH.$$

It was also shown that when dry ammonia is passed into boiling methylic salicylate, dimethylamine is produced, but no phenol is formed.

In the earlier papers a provisional theory was put forward as to the manner in which the reaction between aniline and methylic salicylate took place. Subsequent investigation has shown that this theory is inadequate.

The work described in the present communication was undertaken mainly in the hope of throwing light on the mechanism of the synthesis.

---

[1] This JOURNAL, **24**, 52; **24**, 276–281.

It was in the first place necessary to know precisely what products were formed when dry ammonia reacts with methylic salicylate. The volatile one had been already shown to be dimethylamine. The investigation was therefore in this instance confined to the non-volatile substances which remain dissolved in the excess of methylic salicylate.

By passing ammonia into the boiling ester for twenty hours, a sufficient quantity of these was obtained for investigation. The mixture was separated into its constituents by extraction with hot alcohol, and on cooling the soluble substance crystallized. It melted at 139°, gave a blue-purple color with ferric chloride, and had the same crystalline form as salicylamide, with which it was clearly identical.

The substance insoluble in alcohol was crystallized from benzene. It forms greenish-yellow needles and melts above 280°. Both its appearance and general behavior support the idea that it is polysalicylic nitrile. Limpricht[1] obtained this substance by heating salicylamide to 270°; Miller[2] states that it melts at 296° to 299°. The amount produced in the reaction at present under consideration is quite small.

It may therefore be stated that ammonia acts on methylic salicylate at its boiling-point to produce dimethylaniline and salicylicamide: the latter is then partly converted into polysalicylicnitrile. The non-production of phenol in the reaction seemed a noteworthy point, making it at first difficult to see what mechanism it might have in common with the production of alkylanilines. Further study has, however, removed the difficulty.

The action of dry ammonia gas on ethylic salicylate and on isoamylic salicylate was next studied. These have been shown to act much more slowly upon aniline than does methylic salicylate. When ammonia gas was passed into the esters, at their boiling-point, during four hours, it was found that the reaction had not proceeded to any appreciable extent. The ethylic ester gave a trace of what appeared to be polysalicyl nitrile, but in the case of neither ester was there the slightest evidence of the production of an amine, and the work in this direction was suspended. The velocity of these reactions is clearly decreased by the increasing mass of the alkyl group involved.

---

[1] Ann. Chem. (Liebig), 98, 261.

[2] Ber. d. chem. Ges., 22, 2798.

The action of aniline on methylic benzoate was next studied. These bodies, after being carefully dried, were boiled together for six and a half hours. Two experiments were made: In one, the substances were present in equimolecular proportions; in the other, an excess of aniline was employed. In both cases the sole product was benzanilide; neither methylaniline nor dimethylaniline was produced. It is also noteworthy that the absence of hygroscopic moisture did not diminish the production of the anilide, as is the case when aniline and methylic salicylate react.

An attempt was next made to see whether the reverse reaction took place. Benzoic acid and dimethylaniline (in the proportion of 4 molecules of the former to 1 of the latter) were boiled together for nine hours. From the resulting mixture a neutral liquid was obtained, which gave, when distilled, methylic benzoate and a small tarry residue. It was not possible to show, in the latter, the presence of either benzanilide or methylbenzanilide. Probably any aniline or methylaniline formed in the reaction would finally appear in that form. Failure to detect their presence may be fairly attributed to the slight amount formed, and to their liability to be converted into resins under the conditions of the experiment. Attempts to show that aniline or methylaniline accompanied the unchanged dimethylaniline were equally unsuccessful.

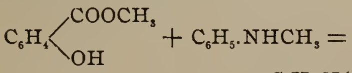
It seemed to the writer that a basis was now provided on which a complete explanation of the reactions so far studied might rest. It may be supposed that we have to do with a reversible reaction which is represented by the following equations:

$$(1)\ \mathrm{R.COO.R' + C_6H_5.NH_2 = R.COOH + C_6H_5.NHR'};$$

$$(2)\ \mathrm{C_6H_5NHR' + RCOOH = C_6H_5.NH_2 + R.COOR'}.$$

In the case of methylic benzoate and aniline, it would then appear that the velocity of the reaction (1) is much less than that of reaction (2). Thus, supposing the former to occur to any extent, it would be quickly reversed, since the benzoic acid would only be removed slowly from the sphere of activity by conversion into benzanilide. Direct evidence that the reaction (2), or one similar to it, does occur is supplied by the formation of methylic benzoate from benzoic acid and dimethylaniline. When an alkyl salicylate and aniline are boiled together the reaction is practically non-reversible; however slowly that represented by equation (1) takes place, it will be quickly followed by the decomposition of the liberated salicylic acid into carbon dioxide and phenol, and that represented by equation (2) cannot, therefore, take place. The reason for the non-production of phenol when ammonia gas acts on boiling methylic salicylate appears to be that, in the presence of an excess of ammonia, the liberated salicylic acid at once forms ammonium salicylate; this, at the temperature of the experiment, is decomposed into salicylamide and water. Part of the amide then further loses water and forms polysalicylic nitrile. It seems that the different course of the reaction is due to the formation of salicylamide being more rapid, under the conditions of the experiment, than is the formation of phenol.

If, however, this view of the general nature of the reaction is correct, it follows that tertiary amines might also be produced. The reaction



$$C_6H_4\left\langle\begin{matrix}COOCH_3\\OH\end{matrix}\right. + C_6H_5.NHCH_3 = C_6H_5.N(CH_3)_2 + C_6H_5OH + CO_2$$

might take place slowly, but there would be no obvious reason why it should not take place at all.

Hitherto no formation of a tertiary amine by this reaction had been observed. The conditions had, however, always been such as to favor the formation of a secondary amine. In all experiments the base had been in excess of the ester. An experiment was therefore made to determine whether in *all* circumstances secondary amines only are produced. Methylic salicylate and aniline, in the proportion of two molecules of the former to one of the latter, were boiled together for six hours. The resulting basic oil consisted of dimethylaniline, without any trace of either unchanged aniline or of methylaniline.

A further consequence of the theory of this reaction is that other alkyl esters should yield alkylanilines when boiled with aniline, provided that the acid from which they are derived is unstable at the temperature of the experiment. When, however, the acid is stable, we need expect no such reaction to take place, or should it do so, it would be more or less completely reversed. Limpricht[1] showed that when the three hydroxybenzoic acids are distilled with aniline, the ortho and the para acids are almost completely converted into phenol, while the meta acid gives no phenol, but a good yield of *m*-hydroxybenzanilide. From this it follows that esters of *p*-hydroxybenzoic acid should give alkylanilines, but that *m*-hydroxybenzoic esters should not do so.

Methylic *p*-hydroxybenzoate was boiled for four hours with three molecular proportions of aniline. The products were phenol, unchanged ester, aniline, and dimethylaniline. No methylaniline was found. Under the same circumstances (an excess of aniline), the salicylic ester gives phenol and methylaniline.[2] None of the ester remains undecomposed, and no dimethylaniline is formed. We thus see that methylic salicylate reacts more rapidly with aniline than does methylic *p*-hydroxybenzoate, but the production of dimethylaniline by the latter tends to show that methylaniline is more quickly acted upon by it than by methylic salicylate.

Methylic *m*-hydroxybenzoate does not appear to have been hitherto described. It is readily prepared by Fischer's method; it may be purified by crystallization from a mixture of benzene and light petroleum, and is deposited in bunches of beautiful white needles. Its melting-point is 70°.

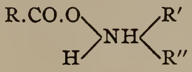
Methylic *m*-hydroxybenzoate was boiled for six hours with three molecular proportions of aniline. The non-basic products were unchanged ester and *m*-hydroxybenzanilide. After removing the excess of aniline from the basic products, the residue consisted of a small amount of an oil, which did not yield methylacetanilide when treated with acetyl chloride. It had no constant boiling-point; the larger portion distilled between 230° and 250°. It was not, therefore, dimethylaniline, the boiling-point of which is 191° to 193°. Probably it consisted of the concentrated impurities from the 59 grams of aniline employed; the quantity obtained was too small for further investigation.

---

[1] Ber. d. chem. Ges., **22**, 2907.

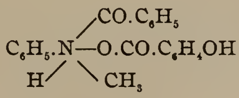
[2] This JOURNAL, **24**, 52.

The facts so far investigated seem, in the main, to lead to the conclusion that the production of amines by salicylic esters merely depends on the rapid removal, under the experimental conditions, of salicylic acid. An analogy is readily seen between the action of alkyl esters and of alkyl haloids on ammonia or on amines. The greater ease with which alkyl haloids react is probably attributable to the facility with which the haloid acid produced in the reaction is neutralized by the formation of stable ammonium salts. Analogy suggests the formation of similar unstable intermediate compounds of the type

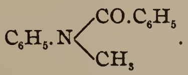


in this synthesis.

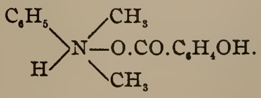
Apart from such analogy, the only evidence bearing upon the point is furnished by the fact that no reaction could be observed when methylic salicylate and benzanilide or isoamylic salicylate and acetanilide were boiled together during five and six hours, respectively. This is readily understandable if it be remembered that the formation of the compound



must precede that of the compound



It is easily seen that the former would be produced with much greater difficulty than would, for example, the compound

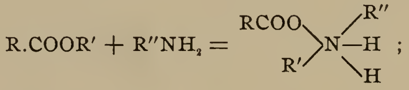


It seems probable, also, that the formation of these substituted ammonium salts precedes the formation of amides and anilides from esters.

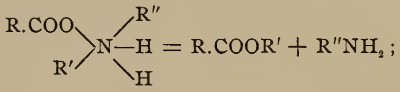
It is, at first sight, conceivable that the formation of an anilide from an ester might depend entirely on the presence of traces of water (as was shown to be the case with salicylanilides[1]), and that the water acts by first hydrolyzing the ester. In such case the reaction would be represented as follows:

$$\mathrm{R.COOCH_3 + H_2O = R.COOH + CH_3OH;}$$
$$\mathrm{R.COOH + C_6H_5NH_2 = R.CONH.C_6H_5 + H_2O.}$$

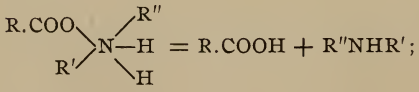
Such an idea is, however, set aside when one sees that dried methylic benzoate and anhydrous aniline give a fair yield of anilide when boiled together in a dry apparatus. On this view the possible actions of an ester on a primary amine would be represented as follows:

(1) 

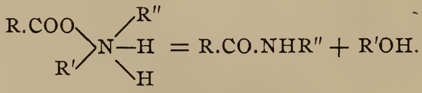
$$\mathrm{R.COOR' + R''NH_2 = \begin{array}{l}\mathrm{RCOO}\diagdown \\ \mathrm{R'}\diagup\end{array}\!\mathrm{N}\!\begin{array}{l}\diagup\mathrm{R''} \\ -\mathrm{H} \\ \diagdown\mathrm{H}\end{array};}$$

(2) 

$$\mathrm{\begin{array}{l}\mathrm{R.COO}\diagdown \\ \mathrm{R'}\diagup\end{array}\!\mathrm{N}\!\begin{array}{l}\diagup\mathrm{R''} \\ -\mathrm{H} \\ \diagdown\mathrm{H}\end{array} = R.COOR' + R''NH_2;}$$

(3) 

$$\mathrm{\begin{array}{l}\mathrm{R.COO}\diagdown \\ \mathrm{R'}\diagup\end{array}\!\mathrm{N}\!\begin{array}{l}\diagup\mathrm{R''} \\ -\mathrm{H} \\ \diagdown\mathrm{H}\end{array} = R.COOH + R''NHR';}$$

(4) 

$$\mathrm{\begin{array}{l}\mathrm{R.COO}\diagdown \\ \mathrm{R'}\diagup\end{array}\!\mathrm{N}\!\begin{array}{l}\diagup\mathrm{R''} \\ -\mathrm{H} \\ \diagdown\mathrm{H}\end{array} = R.CO.NHR'' + R'OH.}$$

The above general formulæ may obviously be applied to secondary amines, or to ammonia. As soon as reaction (1) has been brought about, it will depend on the nature of the reacting substances, and the experimental conditions, whether reaction (2), (3), or (4) is the predominant one. For example, when dry methylic salicylate and aniline are boiled together, reaction (3) only takes place; when a trace of water is present reaction (4) proceeds to some extent. When dry ammonia acts on boiling methylic salicylate, reaction (3) is still predominant. If the latter substances react at 100° and in the presence of water and alcohol, then reaction (4) is the only one to occur; when methylic benzoate and aniline are boiled together, reactions (2) and (4) predominate.

---

[1] This JOURNAL, 24, 52.

EXPERIMENTAL.

Ammonia Gas and Methylic Salicylate.

Dry ammonia was passed into boiling methylic salicylate for about twenty hours. After cooling the liquid, light petroleum was added, and the crystals which separated were filtered off. The greater part of the mother-liquid was then distilled over, and more crystals separated from the residue. These were combined with those previously deposited; the mixture obtained was extracted with hot alcohol and the resulting solution was filtered; crystals deposited from the filtrate when cool, which, by their form, their melting-point (139°), and their behavior towards alcoholic ferric chloride solution, were identified as salicylamide.

That small portion of the mixture which was insoluble in alcohol was dissolved in hot benzene, from which greenish-yellow crystals were deposited on cooling. These melt above 280° and appear to consist of polysalicyl nitrile. This body was obtained by Limpricht,[1] when salicylamide was heated at 270°. According to Miller[2] its melting-point is 296°–299°.

Ammonia Gas and Ethylic Salicylate.

Dry ammonia was passed into boiling ethylic salicylate for about four hours. The escaping gas was collected in water; after neutralizing the solution with hydrochloric acid, no diethylamine or other ethylated ammonia could be discovered. Examination of the residual ester showed only a minute trace of what was probably polysalicyl nitrile (see above).

Ammonia Gas and Isoamylic Salicylate.

An experiment similar to the above was made, using isoamylic salicylate instead of the ethylic ester. No action was observed to have taken place.

---

[1] Ann. Chem. (Liebig), 98, 261.

[2] Ber. d. chem. Ges., **22**, 2798.

Separation of Aniline, Methylaniline, and Dimethylaniline.

In all experiments where this operation was necessary, the method followed was that recommended by A. W. Hofmann.[1] It is briefly described in Beilstein's "Handbuch."[2] The only change introduced was to repeat the treatment of the free bases with dilute sulphuric acid a second, or even a third, time before proceeding to separate the methylaniline and dimethylaniline.

Methylic Benzoate and Aniline.

Methylic benzoate (54.4 grams) was dried over calcium chloride and mixed with an equimolecular proportion of aniline (37.2 grams) which had been dried over sodium. The mixture was boiled for six and a half hours in a dry flask fitted with a reflux condenser. When cool, crystals of benzanilide separated. They melted at 159°, and, when hydrolyzed, gave aniline and benzoic acid. Yield, 8 grams. The filtrate from these crystals was poured into dilute hydrochloric acid and shaken with ether. The latter removed the unchanged methylic benzoate, while all bases were dissolved in the acid liquid. This was then separated, neutralized with sodium hydroxide, and extracted with ether; the ether was distilled off and the residue treated with the object of separating any methylaniline or dimethylaniline formed in the reaction. After removing the aniline only a few drops of oil remained. This became gummy when treated with acetyl chloride, and no methylacetanilide resulted. The amount was too small for further investigation.

It would thus seem that neither methylaniline nor dimethylaniline was formed in this experiment. The residual oil probably consisted of the concentrated impurities originally present in the aniline.

Another experiment, carried out in a similar manner, but using 4.5 molecular proportions of aniline to 1 molecular proportion of methylic benzoate, gave an equally negative result, the products being benzanilide, unchanged ester, and aniline.

---

[1] Ber. d. chem. Ges., 10, 599.

[2] 3te Auf., 2ter Band, 324.

Dimethylaniline and Benzoic Acid.

Four molecular proportions (48.8 grams) of benzoic acid and 1 molecular proportion (12 grams) of aniline, were boiled together for nine hours. The product was dissolved in ether, and the solution repeatedly extracted with a solution of potassium carbonate to remove the excess of benzoic acid. The aniline bases were then removed from the ether by extraction with dilute hydrochloric acid. Once more the ethereal liquid was shaken with a solution of potassium carbonate; it was then dried and the ether removed by distillation on the water-bath. The residue was an oil of which there was so little that an accurate determination of its boiling-point could not be made. It passed over, however, between 150° and 200°, leaving only a tarry residue. It did not mix with water or with concentrated hydrochloric acid. It dissolved on warming with a solution of potassium hydroxide in dilute alcohol. This solution was cooled and acidified with hydrochloric acid. Crystals separated which melted at 120°. They gave both the smell and the characteristic crystalline form of benzoic acid when sublimed. On these grounds it is inferred that the liquid from which they were produced was methylic benzoate, the boiling-point of which is 199°. An unsuccessful attempt was made to isolate aniline or methylaniline from the unchanged dimethylaniline, and it was not possible to demonstrate the presence of benzanilide or methylbenzanilide in the tar which accompanied the methylic benzoate.

Methylic Salicylate and Aniline.

Two molecular proportions of methylic salicylate (50 grams) and 1 molecular proportion of aniline (15 grams) were boiled together for six hours. The product was poured into dilute hydrochloric acid, and the phenol removed by shaking with ether. On neutralizing the acid solution, a base separated which was extracted with ether. After removing the ether it was shown, by the dilute sulphuric acid test, to be free from aniline. No methylacetanilide was formed on treating the base with acetyl chloride. It boiled at 192° to 193° (boiling-point of dimethylaniline 191° to 193°). It is evident that, under these circumstances no methylaniline, but only dimethylaniline, is produced. The yield of purified base was 8.3 grams.

Methylic p-Hydroxybenzoate and Aniline.

These substances were boiled together for four hours, 15.2 grams (1 molecule) of ester and 27.9 grams (3 molecules) of aniline being employed. The product was subsequently distilled. A considerable portion of unchanged ester remained in the distilling flask. The distillate was poured into a solution of potassium hydroxide and extracted with ether. The ethereal layer was separated, the ether distilled, and the residue treated with a view to separating the constituent bases. Aniline was, of course, present in excess; no trace of methyl aniline was found, but a quantity of dimethylaniline (boiling at 191°) was isolated. The weight of this substance finally obtained was 2.4 grams, but the true yield was somewhat greater. Through an accident, about a gram of the base was lost after purification, before it could be weighed.

The alkaline liquid, from which the bases were extracted, was acidified and extracted with ether. From this extract phenol and *p*-hydroxybenzoic acid were obtained. The latter doubtless was formed by hydrolysis of that portion of the ester which distilled over. Phenol was, as usual, identified by its smell and by the formation of its tribromderivative.

Methylic m-Hydroxybenzoate and Aniline.

Three molecular proportions (59.2 grams) of aniline were boiled for six hours with 1 molecular proportion (27.9 grams) of methylic *m*-hydroxybenzoate. The product was then distilled, leaving a tarry residue. Bases were extracted from the distillate by dissolving it in ether and shaking with dilute hydrochloric acid. That part remaining dissolved in the ether was found to consist of *m*-hydroxybenzanilide and unchanged methylic *m*-hydroxybenzoate; no phenol could be detected. The acid solution was made alkaline and the free bases extracted with ether. Aniline was separated in the usual manner.

Acetyl chloride and water caused no precipitation of methylacetanilide. On the addition of alkali a few drops of an oil separated. It was extracted with ether and carefully examined, but did not appear at all similar to dimethylaniline. It did not possess a constant boiling-point, but the greater part boiled between 230° and 250°. The quantity obtained was, however, so small that these points even are uncertain. It seems probable that it is a mixture of impurities originally present in the aniline.

Methylic m-Hydroxybenzoate.

This compound appears not to have been hitherto described. It is readily prepared by Fischer's esterification method, using the same concentration of sulphuric acid in methyl alcohol as for the preparation of methylic salicylate. The yield is very good. The ester is readily purified by crystallization from a mixture of benzene and light petroleum. It forms clusters of magnificent long, white needles, and melts at 70°.

Methylic Salicylate and Benzanilide.

These substances were boiled together for five hours, in the proportion of 2 molecules of the former to 1 of the latter. The mixture was subsequently hydrolyzed by boiling with a solution of potassium hydroxide. Aniline was liberated, but no methylaniline could be detected, thus showing that no methylbenzanilide had been formed.

Isoamylic Salicylate and Acetanilide.

Two molecular proportions of isoamylic salicylate and 1 molecular proportion of acetanilide were boiled together for six hours. The product was treated as in the preceding experiment. The result showed that no isoamylacetanilide had been formed.

Methylic Salicylate and Ammonia in the Presence of Dilute Alcohol.

Several grams of methylic salicylate were mixed with an excess of strong aqueous ammonia (sp. gr. 0.9), and sufficient alcohol to dissolve the ester. The mixture was heated in a pressure bottle, at 100°, for three hours. After cooling, the product was acidified, and the salicylamide was extracted with ether. On evaporating the aqueous layer, ammonium chloride separated, but no methyl derivative could be detected.

HAVEMEYER HALL,
COLUMBIA UNIVERSITY.

NOTES.

Argon and Its Companions.

Following is an abstract of a paper by William Ramsay and Morris W. Travers, read before the Royal Society, November 15, 1900, and published in the Chemical News of November 30:

The discovery of krypton and neon was announced to the Royal Society in the early summer of 1898; and, subsequently, atmospheric air was found to contain a heavier gas to which the name of xenon was applied. Mr. Baly, in the autumn of the same year, called attention to the presence of helium lines in the spectrum of neon, an observation which confirms that made by Professor Kayser, of Bonn, and by Dr. Friedländer, of Berlin.

At the same time we imagined we had obtained a gas with a spectrum differing from that of argon, and yet of approximately the same density. To this gas we gave the name metargon. It has now been found that the presence of the so-called metargon is to be accounted for by the fact that in removing oxygen from the mixture of these gases, which was then in our hands, phosphorus containing carbon was employed; this mixture, when burned in oxygen, yields a spectrum to some extent identical with that furnished by carbon monoxide, but differing from it inasmuch as lines of cyanogen are also present. We have no doubt that the so-called metargon, the spectrum of which is visible only at high pressure, and only when impure phosphorus has been employed to remove oxygen, must be attributed to some carbon compound. In spite of numerous experiments we have not yet succeeded in producing any gas in quantity which yields this composite spectrum. It is only to be obtained by a mixture of carbon monoxide with cyanogen.

To obtain the heavier gases, krypton and xenon, a large amount of air was allowed to evaporate quietly; the residue was freed from oxygen and nitrogen, and then consisted of a mixture of krypton, xenon, and argon, the last forming by far the largest portion of the gas; this mixture was liquefied by causing it to flow into a bulb immersed in liquid air, and the bulk of the argon was removed as soon as the temperature rose, the krypton and the xenon being left behind. By many repetitions of this process we were finally successful in separating these three gases from each other. While krypton has a considerable vapor-pressure at the temperature of boiling air, the vapor-pressure of xenon is hardly appreciable, and this afforded a means of finally separating these two gases from one another; in the complete paper the operations necessary to separate them are fully described.

For neon the process of preparation was different. The air liquefier furnished a supply of liquid air; the gas escaping from the liquefier consisted largely of nitrogen; this mixture was liquefied in a bulb immersed in the liquid air which the machine was making. When the bulb had been filled with liquid nitrogen a current of air was blown through the liquid until some of the gas had evaporated. That gas was collected separately, and deprived of oxygen by passage over red-hot copper; it contained the main portion of the neon and the helium present in the air. The remainder of the nitrogen was added to the liquid air used for cooling the bulb in which the nitrogen was condensed. Having obtained a considerable quantity of this light nitrogen it was purified from that gas in the usual manner, and the argon containing helium and neon was liquefied. By fractional distillation it was possible to remove the greater portion of the helium and neon from this mixture of gases, leaving the argon behind. Many attempts were made to separate the helium from the neon. Among these was fractional solution in oxygen, followed by a systematic diffusion of the two gases; but it was not found possible to raise the density of the neon beyond the number 9.16, and its spectrum still showed helium lines. It was not until liquid hydrogen, made by an apparatus designed and built by one of us (M. W. T.), had been produced in quantity, that the separation was effected; the neon was liquefied, or perhaps solidified, at the temperature of boiling hydrogen, while the helium remained gaseous. A few fractionations served to produce pure neon; we did not attempt to separate the helium in a pure state from this mixture.

That these are all monatomic gases was proved by determination of the ratio of their specific heats by Kundt's method. The physical properties which we have determined are the refractivities, the densities, the compressibilities at two temperatures, and of argon, krypton, and xenon the vapor-pressures and the volumes of the liquids at their boiling-points.

The results are shown in the table on next page.

The compressibilities of these gases also show interesting features. They were measured at two temperatures, 11°.2 and 237°.3; the value of P V for an ideal and perfect gas at 11°.2 is 17,710 meter-cubic centimeters, and at 237°.3 it is 51,800. This is, of course, on the assumption that the prod-

	Helium.	Neon.	Argon.	Krypton.	Xenon.
Refractivities (Air = 1)	0.1238	0.2345	0.968	1.449	2.364
Densities of gases (O=16)	1.98	9.97	19.96	40.88	64
Boiling-points at 760 mm.	?	?	86°.9 abs.	121°.33 abs.	163°.9 abs.
Critical temperatures	?	Below 68° abs.	155°.6 abs.	210°.5 abs.	287°.7 abs.
Critical pressures	?	?	40.2 meters	41.24 meters	43.5 meters
Vapor-pressure ratio	?	?	0.0350	0.0467	0.0675
Weight of 1 cc. of liquid	?	?	1.212 grams	2.155 grams	3.52 grams
Molecular volumes	?	?	32.92	37.84	36.40

uct remains constant whatever be the variation in pressure. Now with hydrogen at 11°.2 C. the product increases with the rise of pressure; with nitrogen, according to Amagat, it first decreases slightly and then increases slightly. With helium the increase is more rapid than with hydrogen; with argon there is first a considerable decrease, followed at very high pressures by a gentle increase, although the product does not reach the theoretical value at 100 atmospheres' pressure; with krypton the change with rise of pressure is a still more marked decrease, and with xenon the decrease is very sudden. At the higher temperature the results are more difficult to interpret; while nitrogen maintains its nearly constant value for P V, helium decreases rapidly, then increases, and the same peculiarity is to be remarked with the other gases, although they do not give the product of P V coinciding with that calculable by assuming that the increase of P V is proportional to the rise of absolute temperature.

That the gases form a series in the periodic table, between that of fluorine and that of sodium, is proved by three lines of argument:

(1) The ratio between their specific heats at constant pressure and constant volumes is 1.66.

(2) If the densities be regarded as identical with the atomic weights, as in the case with diatomic gases, such as hydrogen oxygen, and nitrogen, there is no place for these elements in the periodic table.

The group of elements which includes them is:

Hydrogen 1	Helium 4	Lithium 7	Beryllium 9
Fluorine 18	Neon 20	Sodium 23	Magnesium 24
Chlorine 35.5	Argon 40	Potassium 39	Calcium 40
Bromine 80	Krypton 82	Rubidium 85	Strontium 87
Iodine 127	Xenon 128	Caesium 133	Barium 137

(For arguments in favor of placing hydrogen at the head of the fluorine group of elements, see Orme Masson, Chemical News, 1896, Vol. **73**, p. 283.)

(3) These elements exhibit gradations in properties such as refractive index, atomic volume, melting-point, and boiling-point, which find a fitting place on diagrams showing such periodic relations. Some of these diagrams are reproduced in the original paper. Thus the refractive equivalents are

found at the lower apices of the descending curves; the atomic volumes, on the ascending branches, in appropriate positions; and the melting- and boiling-points, like the refractivities, occupy positions at the lower apices.

Although, however, such regularity is to be noticed, similar to that which is found with other elements, we had entertained hopes that the simple nature of the molecules of the inactive gases might have thrown light on the puzzling incongruities of the periodic table; that hope has been disappointed. We have not been able to predict accurately any one of the properties of one of these gases from a knowledge of those of the others; an approximate guess is all that can be made. The conundrum of the periodic table has yet to be solved.

The Liquefaction of Hydrogen.

At a meeting of the Physical Society of London, a paper on the above subject was read by Dr. M. W. Travers. An abstract of the paper is given herewith:

These experiments were undertaken in order to provide liquid hydrogen in sufficient quantity for the separation of neon from the helium with which it is usually mixed. The separation is effected by cooling the gases to the temperature of hydrogen boiling at atmospheric pressure. The principles and conclusions do not differ from those of Dewar, but as the production of liquid hydrogen is neither difficult nor costly, an account of the experiments is given.

In 1884, Wroblewski showed that strongly cooled and compressed hydrogen, on being allowed to expand, formed mist or spray in the tube; and, later, Olszewski repeated these experiments on a larger scale, and determined the temperature of the liquid. Other methods of liquefying hydrogen have been suggested by Lord Rayleigh and Kammerlingh Onnes. In the case of many gases a fall of temperature takes place on free expansion, but under ordinary circumstances the temperature rises in the case of hydrogen and helium. The principle of free expansion was first applied by Hampson and Linde to the liquefaction of air. Within the last two years Dewar has shown that at a temperature close to —200° C. hydrogen behaves as an imperfect gas, and becomes cool when allowed to expand. This principle has been applied by Dewar to the liquefaction of hydrogen in quantity. In the author's experiments, hydrogen, under a pressure of 200 atmospheres, passes through a coil which is cooled to —80° C. by a mixture of solid carbonic acid and alcohol. It then enters another coil contained in a chamber which is continually replenished with liquid air. The lower portion of the coil passes into another chamber, which is closed and communicates through a pipe with an exhaust pump. Liquid air flows continuously from the first chamber into the second through a pin valve controlled by a lever. The liquid air, boiling under a pressure of 100 mm. of mercury, lowers the temperature to —200° C. The gas then passes into a regenerator coil, which is enclosed in a vacuum vessel, and, expanding at a valve, passes upwards, through the interstices of the coil and the annular space surrounding the chambers through which the gas first passes, to an outlet whence it can return to the main supply pipe. The liquid which separates from the gas is ultimately collected in a vacuum vessel.

The apparatus, with the exception of the compressor, motor, and Hampson air liquefier, is comparatively inexpensive. About $250 is required for the additional apparatus, and each time liquid hydrogen is made involves a further expenditure of about $5.00.

Centenary Commemoration Lecture at the Royal Institute of Great Britain.

The Centenary Lecture was given by Professor Dewar last June, and has recently been published. The lecturer showed a large number of extremely interesting experiments, and some account of these is given in the abstract herewith communicated:

This large spherical double-walled and silvered vacuum vessel contains 1 liter of liquid hydrogen. You observe it is lifted out of a large cylindrical vessel full of liquid air. In order to diminish the rate of evaporation it is necessary to surround the vessel in which the hydrogen is collected with liquid air. Under such conditions the rapidity of evaporation is about the same as that of liquid air when kept in a similar vessel in the ordinary way. In order to prove that hydrogen is present in the liquid form, the simplest experiment is to remove the cotton-wool plug which takes the place of a cork, and insert a metallic wire, to the end of which is attached a ball of asbestos for the purpose of absorbing the liquid. On bringing it quickly into the air and applying a light, it burns with the characteristic appearance of the hydrogen flame. The liquid can readily be poured from one variety of vacuum vessel into another, so that by means of this unsilvered cylindrical form the appearance of the liquid and other experiments may be projected on a screen. The liquid hydrogen appears in gentle ebullition and is perfectly clear, only there is a white solid deposit in the bottom of the tube, which is really solid air. This may be shown by removing for an instant the cotton-wool stopper, when you see a snow of solid air falling in the liquid. It is easy to arrange a method of carrying liquid hydrogen in a small vacuum vessel in such a way as to prevent the access of air. For this purpose the vacuum vessel, after it has been filled by dipping it into the main supply by means of a supporting wire, is surrounded with a glass envelope, which becomes filled with an atmosphere of hydrogen gas constantly maintained, thereby preventing the access of air. That the density of the liquid is very small and is altogether unlike liquid air is shown by dropping small pieces of cork, which float readily in the latter liquid, but sink instantly in the hydrogen. The real density of the liquid is only 1/14 that of water, so that it is by far the lightest known liquid. This small density explains the rapidity with which the liquid is cleared on the entrance of the air snow. The relative smallness of the gas bubbles produced in the actively-boiling liquid which causes an appearance of opalescence, is really due to the small surface-tension of the liquid hydrogen. The coefficient of expansion of liquid hydrogen is some five times greater than that of liquid oxygen, and is comparable with that of carbonic acid, about 5° from its critical point. The latent heat of evaporation is about 190 units, and the specific heat of the liquid is very high, and so far as my experiments go, leads me to the value 6. This is in very marked contrast to the specific heat of liquid oxygen, which is about 0.5. The extraordinary lowness of its boiling-point is at once apparent by cooling a piece of metal in the liquid and then removing it into the air, when it will be seen to condense for a moment solid air on its surface which soon melts and falls as liquid air. This may be collected in a small cup, and the production of oxygen demonstrated by the ignition of a red-hot splinter of wood after the chief portion of the nitrogen has evaporated. If a long piece of quill tubing sealed at one end, but open at the other, is placed in the liquid, then the part that is cooled rapidly fills with liquid air. On stopping any further entrance of air by closing the end of the tube, the liquid air quickly becomes solid, showing in the interior a hollow spindle from contraction, in passing from the liquid into the solid form. On bringing the tube containing the solid from the liquid hydrogen-bath into the air, we observe liquid air running from the surface while the solid air inside is seen to melt. Here is a tube into which liquid oxygen has been poured. On placing it in liquid hydrogen it freezes to a clear blue ice. Liquid nitrogen under similar circumstances forms a colorless ice. If instead of an open tube in free air we employ a closed vessel of about 1 liter capacity to which the quill tube is attached, then, on repeating the experiment, the same results follow, only the volume of the liquid air formed agrees with the total quantity present in the vessel. This suggests that any left in the closed vessel must have a very small pressure. This is confirmed by attaching a mercurial gauge to any vessel containing air, when it will be seen the vacuum produced by hydrogen cooling is equal to that of a Torricellian vacuum. To read such a high exhaustion the solid oxygen and nitrogen, at the boiling-point of hydrogen, must be practically non-volatile or have an exceedingly small vapor-pressure. If the ordinary air contains free hydrogen, helium, etc., which are non-condensable in this way of working, then the vacuum would not be so high as with pure oxygen or nitrogen. This method may be used to separate the incondensable gases from the air. Such air vacua, when examined spectroscopically, show the lines of hydrogen, helium, and neon. We may now employ this process to produce high vacua, and test their exhaustion by the character of the electric discharge. Vacuum tubes which have been prepared in this way show extraordinary resistance to the passage of the electric discharge; they also show the marked phosphorescence of the glass, characteristic of Crookes' tubes. It is, however, the rapidity with which such high exhaustions can be attained that is so interesting. You will observe that this large Geissler tube, previously exhausted to some 3 inches' pressure, will, when the end part is immersed in liquid hydrogen, pass through all the well-known changes in the phases of striation—the glow on the poles; the phosphorescence of the glass—in the space of a fraction of a minute. From this it follows that theoretically we need not exhaust the air out of our double-walled vessel when liquid hydrogen has to be stored or collected. This makes a striking contrast to the behavior of liquid air under similar circumstances. The rapid exhaustion caused by the solidification of the air on the surface of a double-walled unexhausted test-tube, when liquid hydrogen is placed in it, may be shown in another way. Leave a little mercury in the vessel containing air, just as if it had been left from making a mercurial vacuum. Now we know mercury, in such a vacuum, can easily be made to distil at the ordinary temperature when we cool a part of the vessel with liquid air, so that we should expect the mercury in the unexhausted test-tube to distil on to the surface cooled with the liquid hydrogen. This actually takes place. A rough comparison of the relative temperatures of boiling hydrogen and oxygen may be made by placing two, nearly identical, hydrogen gas thermometers operating at constant pressure side by side and cooling each with one of the liquids. It will be seen that the contraction in the thermometer, cooled with liquid hydrogen, elevates the liquid some six times higher than that of the corresponding liquid column of the thermometer placed in the liquid oxygen. A constant-volume hydrogen thermometer gave the boiling-point of 21° absolute or 252° C., and a similar helium thermometer gave the same result. The critical temperature is about 32° absolute or —241° C., and the critical pressure about 15 atmospheres. If a closed vessel is full of hydrogen gas at atmospheric pressure, then, unlike the air vessels, it shows no condensation when a part of it is cooled in liquid hydrogen. To produce liquefaction we must increase the pressure of the gas, or reduce the boiling-point of the liquid hydrogen by exhaustion. Pure hydrogen liquefied in a closed vessel is perfectly clear, showing no trace of color or any appearance of absorption bands in the position of the spectrum lines. Electric sparks passing in the liquid when examined with the spectroscope show the ordinary line spectrum without any reversals. The vapor of boiling hydrogen is about fifteen times denser than that of the ordinary gas, thus bringing it up to the density of air. The liquid hydrogen, at its boiling-point, is about sixty times denser than the vapor coming off. In the case of oxygen the density of the liquid is 255 times that of the vapor at its boiling-point.

If a piece of cotton wool in the form of a little ball is attached to a thread, placed in liquid hydrogen, and then brought into the magnetic field, it is found to be strongly magnetic. This is simply due to the condensation of solid and liquid air in the pores of the wool. This substance we know is magnetic on account of the oxygen it contains. Pure liquid hydrogen is not magnetic, but when the solid air snow is in suspension in the fluid, then the magnetic character of the latter becomes apparent when the vessel is placed in the magnetic field.

All the phosphorescent effects produced at low temperatures formerly described are intensified at the much lower temperature of boiling hydrogen. To stimulate phosphorescence at the temperature of liquid air, ultra-violet light had to be employed, and then the solid body, organic or inorganic, allowed to rise in temperature. It was during the rise of temperature that the marked luminous emission took place. Among inorganic bodies the platinocyanide of ammonia is very remarkable in this respect, and generally the group in organic chemistry known as the ketonic bodies. In the case of bodies cooled in liquid hydrogen, it appears that some show phosphorescence by simple stimulation with the light coming from an ordinary carbon filament electric lamp. The light in this case coming through glass contains only, we may say, the visible spectra, so that the ultra-violet rays are not now essential. It is strange to find photographic action still relatively considerable. At the boiling-point of liquid air the photographic intensity is reduced by 80 per cent of the value at the ordinary temperature. The photographic effect on a sensitive film immersed in liquid hydrogen as compared with the same placed in liquid air is as 1 : 2, so that 10 per cent of the action at ordinary temperatures still remains. As every kind of chemical action so far examined is non-existent at this extreme temperature, these experiments suggest that the cause of the photographic action may be essentially physical. No better illustration could be given of the rapid diminution of chemical action at low temperatures than to remind you that fluorine gas, the most active elementary body, under such conditions, may be liquefied and kept in glass vessels.

The effect of a temperature of 21° absolute on the electric resistance of the pure metals is a problem of great interest. In passing from the melting-point of ice to the boiling-point of hydrogen, pure platinum loses resistance till only 1/40 remains, and in the case of electrolytic copper the remaining resistance is only 1/57 of what it was at starting. Such results suggest the approach to the condition of what may be called relatively perfect electric conductivity as the zero of absolute temperature is approached.

Liquid hydrogen is a non-conductor of electricity, and as regards being an insulator for currents of high potential, it is comparable to that of liquid air. The properties of the liquid we have witnessed in no way suggest the metallic character that chemists like Faraday, Dumas, and Graham anticipated; and, for the future, hydrogen must be classed with the non-metallic elements.

The liquefaction of hydrogen has been the consequence of some ten years' devotion to low temperature research. To many it may seem that the results have been indeed costly in more ways than one. The scientific worker who prepares the way for future development in this sort of inquiry generally selects complicated methods, and is attracted or diverted into many by-paths of investigation. He may leave to his successors any credit that may be attached to cheapness and ease of production of the agent of research—results that must invariably follow. Liquid hydrogen is an agent of research which will enable us to examine into the properties of matter at the lowest-maintained temperature ever reached by man. Much work has still to be accomplished. One of the most fascinating problems of the study of low temperatures has been materially advanced. The intervals separating us from the zero of absolute temperature has been reduced to practically 1/4 the value that it stood at when liquid air was the cooling agent. We can produce in pure helium instantaneous temperatures bringing us still nearer the goal. Now we can maintain a temperature within less than 16° of this zero, and the investigator who will make the further attempt to reduce this distance by an equivalent amount, thereby reaching a steady temperature of 4° or 5° absolute, will indeed face a problem of almost insuperable difficulty. Well, let us take comfort in an aphorism of Davy's: "Fortunately for the active and progressive nature of the human mind, even experimental research is only a method of approximation to truth."

Fluosilicic Acid as a Preservative of Manure.

In a recent number of the Chemiker-Zeitung[1] there is an interesting article upon the use of the fluorine compounds formed during the manufacture of superphosphates, which suggest an historical analogy with another member of the same group. In the early days of the LeBlanc process for the manufacture of soda, the hydrochloric acid was allowed to escape until its injurious effects necessitated the passage of laws compelling its removal from the waste gases. This led to the collection and more general use of the acid until finally the profits of the soda industry were all derived from this former waste product. Similar action has recently been taken in Germany to prevent the liberation of injurious amounts of fluorine compounds, which are generated in the manufacture of the fertilizers, and escape through the chimney. These gases are now passed through a series of wooden chambers in which the gases are exposed to a spray of water, which converts the fluorine compounds into silicic and fluosilicic acids. The latter can be separated and converted into its sodium salt, but no use can be made of large quantities of this compound though the aluminium and magnesium salts have been used to harden limestone and sandstone. It has recently been shown that the fluosilicic acid is a better preservative of manure than gypsum and some other substances, in preventing the loss of nitrogen through its influence on the denitrifying agent. This has led to the introduction of a mixture which will generate the acid slowly when applied to the moist manure. Two substances are used in the preparation of this mixture: one, fuller's earth and similar substances mixed with as much sulphuric acid as can be used without destroying the powdery nature of the substance; the other, a solution of the fluosilicic acid treated with enough dried and ground clay to convert the acid into stable salts. Equal parts of the preparations when mixed and sprinkled over the manure generate the fluosilicic acid.

---

[1] Chem. Ztg., **75**, 795 (1900).

In place of the sulphuric acid, powdered bisulphate might be used and, in place of the saturated clay a powder formed by passing the gases over lime in order to convert the acid into salts. On account of the price of the preparation its successful use on a commercial scale is as yet an open question.

J. E. G.

Ammonium Bromide and the Atomic Weight of Nitrogen.

During a research having for its chief aim the determination of the hydrogen to oxygen ratio by comparing the equivalents of hydrazine, ammonia, and hydroxylamine, A. Scott[1] found that he could not obtain the same equivalent as Stas for ammonium bromide. The value given by Stas is 98.032, while that of the author is 97.996, his highest value being 98.003. This would lower the atomic weight of nitrogen from 14.046 to 14.010, a number much nearer that deduced from the relative densities of oxygen and nitrogen (16 : 14.003).

The bromide used by Stas seems to have contained some impurity, probably platinum, as it turned grayish at 115°, and its grayness increased up to 180°. He was unable to sublime it even in ammonia without its becoming yellow. The ammonium bromide of the author retains its whiteness at 180° and has been sublimed in ammonia, in a mixture of hydrogen with ammonia and in a vacuum, giving the same results before and after sublimation. The silver bromide had the same composition as that of Stas (57.445 per cent of silver).

The equivalent for ammonium chloride was also determined, and found to be 53.516, as against 53.532 (Stas) and 53.486 (Marignac).

The silver used was prepared by the reduction of silver nitrate by means of ammonium formate, and was notably better than a sample prepared with the utmost care by the well-known cuprous ammonium sulphite process.

To test the purity of the silver in the severest way, the precipitated silver bromide was reduced by hydrogen, when identical results were obtained with the silver so prepared.

Asymmetric Optically Active Sulphur Compounds.

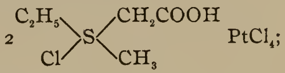
Pope and Peachey have shown that nitrogen and tin compounds, with asymmetric nitrogen and tin atoms respectively, possess optical activity which is to be referred to such asymmetry.

---

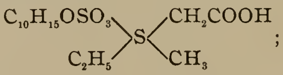
[1] Proceedings of the Chemical Society (London), **16**, 229.

In the case of sulphur compounds many unsuccessful attempts have been made to arrive at the space relations of the groups in sulphonium compounds. The authors mentioned above were unsuccessful in their first attempts to obtain optically active sulphonium compounds. But they found later that they could obtain an optically active double chloride with platinum the formula of which is given below, and besides this they have been able to obtain two other optically active sulphur compounds of the general formula SX_4 which they say are comparable with optically active carbon compounds. In these sulphur compounds, as in the carbon compounds, they consider the sulphur atom to be at the center of a tetrahedron, and the four different groups situated at the apexes. The following formulas represent the three optically active sulphur compounds investigated by these workers:

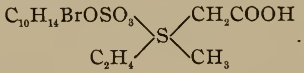
d-Methylethylthetine platinichloride,



d-methylethylthetine *d*-camphorsulphonate,



d-methylethylthetine *d*-bromcamphorsulphonate,



J. C. W. F.

REVIEWS.

DIE AETHERISCHEN OELE, VON E. GILDEMEISTER UND FR. HOFFMANN, Bearbeitet im Auftrage der Firma Schimmel & Co., in Leipzig. Berlin: Julius Springer, 1899. 919 pp.

THE VOLATILE OILS, BY E. GILDEMEISTER AND FR. HOFFMANN, Authorized translation by EDWARD KREMERS. Milwaukee: Pharmaceutical Review Pub. Co., 1900. 733 pp.

Dr. Hoffmann is well-known in this country as the former editor of the Pharmaceutical Review, then Die Pharmaceutische Rundschau. From his pen has come the historical introduction, the history of the volatile oils and of the crude materials, and especially the description of the methods used in obtaining American products. The historical introduction includes a history of the spice trade in antiquity and during the middle ages, a history of the volatile oils, and a history of distillation. The last topic is illustrated by many quaint old illustrations, as well as by cuts showing the forms of apparatus used in large modern establishments.

In the second part of the work are considered, the theoretical basis for obtaining oils by fractional distillation, the more commonly occurring constituents, and general methods of examination. The second of these topics includes a very excellent account of the practical results obtained by Wallach, Semmler, Tiemann, Baeyer, Wagner, Kremers, and others in this field, which is one of the most difficult in organic chemistry.

The remainder of the book, including two-thirds of the whole, is given to a consideration of individual oils, of which 422 are included in the original, and 430 in the translation. This portion of the book has been greatly increased in value by the fact that the authors had at their disposal the observations made in the laboratory of Schimmel and Co., during a long series of years. The authors have also shown excellent judgment in the selection of those facts which will be of value to the chemist who is interested in pure science, to the manufacturer who is interested in methods of production, and to the dealer who is interested in questions of adulteration.

The German edition is magnificently bound in half morocco and well printed on heavy paper. The translation is also well printed and bound, and both editions are embellished with four colored maps and numerous illustrations.

Dr. Kremers has not only rendered the book into clear and idiomatic English but his studies with Wallach, and his own researches in this field have fitted him to act as an editor as well, and in several places results which have appeared since the publication of the German edition are included in the translation. The historical portion has been slightly condensed but the loss has been more than compensated by the bibliographical notes added at the close. W. A. N.

A HANDBOOK OF INDUSTRIAL ORGANIC CHEMISTRY, adapted for the use of Manufacturers, Chemists, and all interested in the utilization of Organic Materials in the Industrial Arts. By SAMUEL P. SADTLER, PH.D., F.C.S., Consulting Chemist, Professor of Chemistry in the Philadelphia College of Pharmacy and in the Franklin Institute of the State of Pennsylvania, etc. Third revised and enlarged edition. Philadelphia: J. B. Lippincott Company. 1900. pp. xviii + 543.

This work appears in substantially the same form as in the second edition, of 1895, but has undergone revision, involving some omissions and rather more considerable additions. Thus, notice is introduced of the treatment of cottonseed and other non-drying or half-drying oils by blowing air through them, to increase viscosity and improve them as lubricants; and, in the chapter on artificial dye-stuffs, a number of the newer dyes are noticed which did not appear in the earlier editions. The general arrangement is based on the raw materials used, instead of on the finished products and their applications. This has some decided advantages, but leads also to some difficulties and anomalies. Thus, most of the little said about explosives is connected on to the fats and oils through nitroglycerin, while gun-cotton is treated in a different part of the book under the head of vegetable textile fibers, and picric acid, the manufacture of which is briefly noticed in the chapter on dye-stuffs, is referred to as an explosive at the end of the section on nitroglycerin, while there is no mention of fulminating mercury or of nitrobenzene as an ingredient of "rend-rock." While, under the head of products obtained by destructive distillation, acetic acid is described, as also in connection with fermentation industries (as vinegar), no account is given of the manufacture of oxalic, tartaric, or citric acid. More space might very well have been given to the rapidly growing industry of more or less "synthetic" perfumes, and the artificial production of such interesting substances as vanillin and coumarin might have been described. Pains have been taken to bring up the statistics of production and importation to more recent years as far as returns are available. The general arrangement of each chapter is clear and likely to be useful to the student, the main headings being Raw Materials, Processes of Manufacture, Products, Analytical Tests and Methods, Bibliography, and Statistics.

J. W. M.

DIE GLYKOSIDE. Chemische Monographie der Pflanzenglykoside nebst systematischer Darstellung der künstlichen Glykoside. Von DR. J. J. L. VAN RIJN, Direktor der landwirtschaftlichen Reichsversuchsstation in Mastricht, Holland. Berlin: Verlag von Gebrüder Borntraeger. 1900. pp. xvi + 511.

The author has attempted to bring together into a condensed form the literature of the glucosides, which is scattered throughout a large number of journals, many of which are not within the reach of most chemists. Until this book appeared the best general account of the glucosides was probably that by O. Jacobsen in Ladenburg's "Handwörterbuch der Chemie," but much work has been done in this field of chemistry since this appeared. The first part of the book deals with the artificial glucosides. After a general discussion of the subject, a detailed description is given of the methods of preparation, properties, and reactions of the compounds of the sugars with alcohols, mercaptans, phenols, aldehydes, ketones, oxyacids, and amines. In the second part the natural glucosides are treated. The material has been arranged according to a botanical classification. The methods for the preparation of the compounds in a pure condition, and their reactions and transformations are given in full. When the chemical structure of the glucoside is known it is given together with the structure of the compounds formed by hydrolysis and other decompositions. While the descriptions of the glucosides are complete in all cases, a number of their synthetical derivatives frequently receive but mere mention. The introduction of the melting-points, boiling-points, solubilities, etc., of these substances would have increased the value of the book. No attempt has been made to give a complete bibliography of the subject, but the more important references are given. In addition to a subject index there is an index of the botanical names used throughout the book. The recently published work is described in an appendix which contains references to papers published as late as 1900. The author has succeeded in preparing a book which will no doubt prove of value to chemists, as it is well written and appears to be accurate. The typography and paper of the book, and the general arrangement of the subject-matter are admirable. J. F. N.

AN OUTLINE OF THE THEORY OF THERMODYNAMICS. BY EDWARD BUCKINGHAM. New York: The Macmillan Company.

As the author notes in his preface, he has intended this volume of 200 pages to be a brief outline of the "Theory of Thermodynamics," but not to give more applications than are essential in making the subject-matter clear. It is his intention mainly to fill the gap in thermodynamics between the elementary treatment in college text-books and the modern memoirs which have appeared in recent years, particularly from Gibbs and Duhem. In this attempt the author has been most successful. He begins with an elementary, yet most satisfactory, treatment of thermometry and calorimetry, and a general discussion of the variables to be used in the subject. He then proceeds to discuss the first principles of thermodynamics, applying it to some simple problems of thermochemistry and to the ordinary calorimetric properties of fluid. He then discusses the second law of thermodynamics and gives several satisfactory applications to such problems as the electromotive force of a reversible galvanic cell, the changes of state of a single substance, change of osmotic pressure with the temperature, and so on. The next chapter is devoted to the criterion of equilibrium of thermodynamic conditions, in which the author pays particular attention to the necessity of making a new assumption rather than as trying to deduce the criterion from the first two principles. The next chapter deals with thermodynamic potentials and free energy; and in the closing chapter there is found a remarkably clear statement and explanation of the simplest cases of the phase rule.

The whole book is noteworthy for its clearness of treatment and the successful attempt by the author to distinguish between the facts of experiment and the assumptions made in their explanations. One feels at times that too much space is devoted to simple mathematical processes; but, as the book is intended for students who are not as familiar as they might be with elementary mathematics, this is surely an error in the right direction. On the whole, the book fills the gap so long felt in thermodynamics, and the student on reading it should be able to follow with pleasure and profit the more advanced problems treated by the masters of the science.

J. S. A.

Corrections.

✓ Vol. 24, p. 49, line 13 *for* "$R.NH_3.\overset{\vee}{C}.CO$" *read* "$R.NH_3.O.\overset{\vee}{C}.CO$."

✓ Vol. 24, p. 276, line 2 from bottom, *for* "diamines" *read* "secondary amines".

VOL. XXV. MARCH, 1901. No. 3.

AMERICAN

CHEMICAL JOURNAL

ON THE ACTION OF AROMATIC SULPHONCHLORIDES ON UREA.

BY IRA REMSEN AND W. W. GARNER.

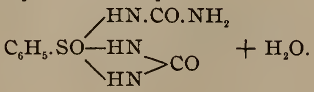
Some time ago Elander[1] found that benzenesulphonchloride acts on urea with elimination of hydrochloric acid to form a product which he represented by the formula

$$C_6H_5.SO.N_4H_5C_2O_2 + H_2O.$$

The action is between one molecule of the sulphonchloride and two of urea, and hydrochloric acid and, apparently, water are eliminated. Elander did not attempt to determine the constitution of the compound but at the time contented himself with making two suggestions. According to one, the compound is formed as a result of the two following reactions:

1. $C_6H_5.SO_2Cl + H_2N—CO—NH_2 =$
$$C_6H_5.SO_2HN.CO.NH_2 + HCl;$$

2. $C_6H_5.SO_2HN.CO.NH_2 + H_2N—CO—NH_2 =$

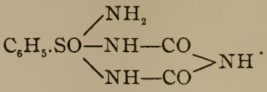


$$C_6H_5.SO\begin{array}{l}\diagup HN.CO.NH_2\\ —HN\diagdown\\ \diagdown HN\diagup\end{array}\!\!>CO \quad + H_2O.$$

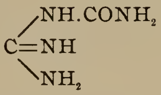
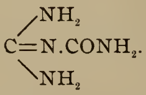
---

[1] Bull. Soc. Chim., 34, 207.

According to the other suggestion the product is a derivative of biuret, which may be represented by the formula



Both of these suggestions are based upon the assumption that an oxygen atom of the sulphone group, SO_2, is eliminated. In view of the fact that the reaction takes place at the temperature of a water-bath, in the presence of urea, it did not appear probable to us that the stable group, SO_2, would under these circumstances give up a part of its oxygen, and these experiments were undertaken with the view of determining the course of the reaction, if possible. The work has been entirely successful and has led to a simple and satisfactory explanation of the reaction. The product is a derivative of guanylurea, which has the constitution represented by the formula

1.  or 2. 

A substance of this constitution is related to urea and its formation from urea is not surprising, though hitherto it has not been obtained in this way. It seems highly probable that in our experiments the sulphonchloride acts, in the first instance, as a dehydrating agent, thus causing the union of two molecules of urea with elimination of water:

$$NH_2—CO—NH_2 + NH_2—CO—NH_2 = C\left\{\begin{array}{l} NH.CO.NH_2 \\ = NH \\ NH_2 \end{array}\right. + H_2O\,;$$

or

$$NH_2—CO—NH_2 + NH_2\text{--}CO—NH = C\left\{\begin{array}{l} NH_2 \\ = N.CO.NH_2 \\ NH_2 \end{array}\right. + H_2O.$$

This eliminated water does not, however, escape as such but reacts with the sulphonchloride to form the sulphonic acid and hydrochloric acid. The hydrochloric acid escapes while the sulphonic acid remains in combination with the base forming a salt which should be represented by the formula

$$C_6H_5.SO_3H.C_2H_6N_4O.$$

This is the *benzenesulphonate of guanylurea*, as we have shown by comparing the substance with the salt made by bringing together benzenesulphonic acid and guanylurea made according to the older methods described in the literature. The experimental details are given in the following paragraphs. The reaction was extended to paratoluenesulphonchloride, orthotoluenesulphonchloride, and to α- and β-naphthalenesulphonchlorides, the results obtained being entirely analogous to those obtained with benzenesulphonchloride.

I. Benzenesulphonchloride and Urea.

1. *Preparation of Guanylurea Benzenesulphonate.*—Twenty-five grams of benzenesulphonchloride and 20 grams of pulverized urea are brought together in a thick-walled beaker and heated in a water-bath to 100°. The mixture soon melts, forming two distinct layers which are mixed by thorough stirring. For a few minutes there is no evidence of action. After a short time the mixture begins to thicken. This is the critical stage of the reaction and requires close attention. Once begun it proceeds rapidly, and the mass solidifies in a few minutes. The beaker should be kept well immersed in the water, and the mass rapidly and thoroughly stirred. Unless these precautions are taken, the reaction becomes violent and the heat evolved at once decomposes any urea that is left. The reaction in this case takes an entirely different course and little or none of the desired product is obtained. As soon as the mass has solidified, it may safely be left to itself. The bath is kept at the boiling temperature and the contents of the beaker occasionally stirred until hydrochloric acid is no longer evolved. After the completion of the reaction, which usually requires from three to four hours, the mass should have the form of a white, crystalline powder. The product thus ob-

tained is allowed to cool and is then dissolved in 200 cc. boiling water. On standing, the product is deposited from the solution in colorless, wart-like aggregates, which can easily be purified by recrystallization from water. By cautious concentration, the mother-liquor yields a second crop of crystals. The sulphonate, when pure, melts at 216° C. (uncorr.). The yield approximates the weight of sulphonchloride used, or 60 to 70 per cent of the theoretical quantity. Analyses gave the following results:

I. 0.2162 gram substance gave 0.2928 gram CO_2 and 0.0921 gram H_2O.

II. 0.2076 gram substance gave 0.2817 gram CO_2 and 0.0846 gram H_2O.

III. 0.1978 gram substance gave 0.1764 gram $BaSO_4$.

IV. 0.1923 gram substance gave 0.1706 gram $BaSO_4$.

V. 0.1858 gram substance gave 35.6 cc. N at 22° C. and 763.4 mm. pressure.

VI. 0.2035 gram substance gave 38.6 cc. N at 19°.3 C. and 757 mm. pressure.

	Calculated for $C_8H_{12}SN_4O_4$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	36.92	36.93	37.0	....	....	....	....
H	4.62	4.76	4.55	....	....	....	....
N	21.54	....	....	....	....	21.73	21.62
S	12.31	....	....	12.25	12.2	....	....

Guanylurea benzenesulphonate obtained in this way always crystallizes in hard, wart-like masses unless allowed to crystallize from very dilute solutions by spontaneous evaporation, when it may be obtained in colorless plates. The sulphonate can be heated in the air to 160° C. without undergoing change, but above this temperature it slowly decomposes. The yield of the sulphonate is about 70 per cent of the theoretical. Guanylurea benzenesulphonate is difficultly soluble in cold water and in alcohol, insoluble in ether and in benzene.

Haag[1] and Baumann[2] have prepared guanylurea and investigated it to some extent. Baumann made it by heating together urea and a salt of guanidine:

$$CO(NH_2)_2 + CH_5N_3 = C_2H_6N_4O + NH_3.$$

[1] Ann. Chem. (Liebig), **122**, 25.

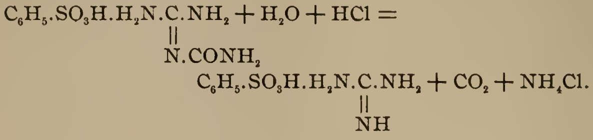
[2] Ber. d. chem. Ges., **7**, 1766.

This has, hitherto, been the most satisfactory method of preparation, but the new method above described gives a much better yield and is simpler. The evidence that our product is a salt of guanylurea was furnished by making the base by Baumann's method and bringing this together with benzenesulphonic acid in solution in water. The salt thus obtained proved to be identical with the product of the action of benzenesulphonic acid on urea. Further, the base was separated from the latter compound, and starting with this, other salts were made and these compared with those described by Haag. The two series were found to be identical.

For the purpose of separating the base from the sulphonate, advantage was taken of the fact established by Haag that, when a solution of a salt of guanylurea is heated with sodium hydroxide and copper sulphate, a characteristic rose-colored copper compound of the base is precipitated. This precipitate was easily formed from the sulphonate. It was filtered off, washed and suspended in water. Through this mixture hydrogen sulphide was passed until the compound was completely decomposed. A solution of the sulphide of the base was thus obtained, and this was used in the preparation of the salts. The salts prepared were the *acid carbonate*, $C_2H_6N_4O.H_2CO_3$, the *oxalate*, $C_2H_2O_4.2C_2H_6N_4O$, the *nitrate*, $C_2H_6N_4O.HNO_3$, the *chlorplatinate*, $(C_2H_6N_4O.HCl)_2PtCl_4$, and the *sulphate*, $(C_2H_6N_4O)_2H_2SO_4$. All of these have characteristic properties.

2. *Action of Hydrochloric Acid on Guanylurea Benzenesulphonate.*—Ten grams of the salt were heated in a sealed tube at 170° to 180° for six hours with hydrochloric acid prepared by mixing 1 part of the concentrated acid with 3 parts of water. Strong pressure was developed during the reaction in consequence of the evolution of carbon dioxide. The resulting product was dissolved in a small quantity of hot water, and, on cooling, a substance crystallized out that proved to be guanidine benzenesulphonate. It appeared in delicate leaflets or large colorless blades, according to the concentration and the rate of cooling of the solution. It was purified by recrystallization from water, and was then found to melt at 206°. It was compared with the salt made by bringing together

guanidine carbonate and benzenesulphonic acid, and the two substances were found to be identical. It is easily soluble in hot water, and somewhat difficultly in cold water. The reaction with hydrochloric acid takes place as represented in the following equation:



$$C_6H_5.SO_3H.H_2N.\underset{\underset{N.CONH_2}{\|}}{C}.NH_2 + H_2O + HCl = C_6H_5.SO_3H.H_2N.\underset{\underset{NH}{\|}}{C}.NH_2 + CO_2 + NH_4Cl.$$

Analyses of the salt gave the following results: I, II, and VII were obtained with the product made from the salt of guanylurea, while III, IV, V, and VI were obtained with the product made from guanidine.

I. 0.2096 gram substance gave 35.3 cc. N at 20° C. and 767 mm. pressure.

II. 0.2036 gram substance gave 35.9 cc. N at 27° and 754 mm. pressure.

III. 0.21 gram substance gave 35.4 cc. N at 19° C. and 760 mm. pressure.

IV. 0.2118 gram substance gave 37.2 cc. N at 26° C. and 756 mm. pressure.

V. 0.1722 gram substance gave 0.1853 gram $BaSO_4$.

VI. 0.1801 gram substance gave 0.1961 gram $BaSO_4$.

VII. 0.2055 gram substance gave 0.2204 gram $BaSO_4$.

	Calculated for $C_6H_5SO_3H.CN_3H_5$.	Found.						
		I.	II.	III.	IV.	V.	VI.	VII.
N	19.35	19.42	19.31	19.38	19.39	....	....	....
S	14.75	....	....	....	....	14.78	14.96	14.73

3. *Action of Nitric Acid.*—To 10 grams of the pulverized material, fuming nitric acid is cautiously added. The reaction is vigorous and the material goes into solution with rapid evolution of fumes. The heat of reaction is sufficient to produce boiling of the solution. To secure a clean reaction a large excess of nitric acid is necessary and the solution is gently heated until there is no further evidence of action. The solution thus obtained is evaporated on the water-bath till the excess of nitric acid is expelled. The residue forms a

thick, gummy mass having a deep-yellow color. This is dissolved in a small quantity of boiling water and, upon cooling, nitroguanidine crystallizes out in an asbestos-like mass of fine needles. The nitroguanidine thus obtained is almost pure and can easily be obtained in pure condition by recrystallizing from water. It melts at 230° C. Ten grams of material treated with 20 cc. of fuming nitric acid gave 2.35 grams of nitroguanidine, which is nearly 60 per cent of the theoretical yield. The product thus obtained was shown by analysis, as well as by the preparation of a number of its derivatives described by Thiele,[1] to be identical with that described in the literature.

Analyses gave the following results :

I. 0.1367 gram substance gave 63.1 cc. N at 15° and 756 mm. pressure.

II. 0.1456 gram substance gave 66 cc. N at 11° C. and 756 mm. pressure.

	Calculated for $CN_4H_4O_2$.	Found. I.	II.
N	53.84	53.78	53.76

With phenol and sulphuric acid a green color was obtained which was changed to a yellowish-green by addition of an alkali.

The *silver salt* was obtained by dissolving the nitroguanidine in a cold solution of alkali and adding an ammoniacal solution of silver nitrate.

Nitroguanidine nitrate was made by dissolving the nitroguanidine in hot concentrated acid. On cooling, it crystallized in blades which melted at 140° C.

Amidoguanidine was obtained by bringing together 5 grams of the nitroguanidine in question, 20 grams of zinc dust, and sufficient ice and water to form a thick paste. To this mixture was added, gradually, 3 grams of diluted glacial acetic acid. When the reduction was complete the filtered solution was evaporated with sufficient nitric acid to expel the acetic acid. From the concentrated solution amidoguanidine nitrate crystallized out, melting at 144° C. By addition of copper acetate to a solution of this salt the characteristic blue *copper*

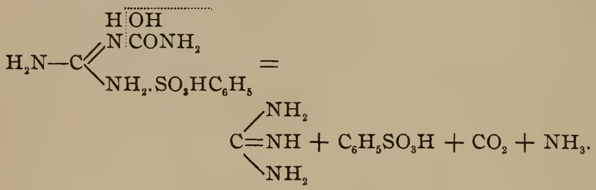
---

[1] Ann. Chem. (Liebig), 273, 140 (1893).

compound was obtained. From a second solution of the salt, upon addition of ammonium picrate, the *picrate* was deposited in well-characterized yellow needles.

According to Limpricht[1] a mixture of the three isomeric mononitrobenzenesulphonic acids results from the nitration of benzenesulphonic acid. By neutralization of the mother-liquor from the nitroguanidine with potassium carbonate a mixture of the three potassium salts is apparently obtained. These salts are difficultly soluble and were obtained in well-crystallized form. No attempt was made to separate them.

The action of nitric acid on the sulphonate is partly represented by the equation :



$$H_2N-C\begin{cases} \overset{H\,\vdots\,OH}{=N\,\vdots\,CONH_2} \\ NH_2.SO_3HC_6H_5 \end{cases} = C\begin{cases} NH_2 \\ =NH \\ NH_2 \end{cases} + C_6H_5SO_3H + CO_2 + NH_3.$$

The guanidine and benzenesulphonic acid thus formed are at once further acted upon by the nitric acid, and nitroguanidine and the nitrobenzenesulphonic acids are formed.

4. *Action of Barium Hydroxide.*—The material is boiled with an excess of barium hydroxide in a flask connected with a return condenser, the upper end of which is fitted with a tube containing soda-lime. The hydrolysis is complete after four to five hours' boiling. The separation of barium carbonate begins at once and ammonia is freely evolved during the operation. The excess of barium is precipitated with carbon dioxide and the filtered solution evaporated to a small volume. Barium benzenesulphonate crystallizes out from the solution in long, colorless prisms.

Analysis gave the following :

I. 0.2146 gram substance gave 0.1061 gram $BaSO_4$.
II. 0.2681 gram substance gave 0.1327 gram $BaSO_4$.
III. 0.343 gram substance lost 0.131 gram H_2O.

---

[1] Ann. Chem. (Liebig), 177, 60.

	Calculated for $(C_6H_5SO_3)_2Ba + H_2O$.	Found. I.	II.	III.
Ba	29.21	29.07	29.1	....
H_2O	3.84	....	....	3.82

To further characterize the product, the barium salt was converted into the potassium salt from which the chloride and the amide were made. The amide thus obtained melted at 152° C. The action of barium hydroxide is in accordance with what we should expect if the product under investigation is a derivative of guanidine. According to Baumann,[1] guanidine is unstable toward barium hydroxide, breaking down into ammonia and urea. Baumann has also shown that other salts of guanylurea conduct themselves in the same way toward barium hydroxide. Ten grams of the material were also boiled with a standard solution of barium hydroxide containing just enough barium to hydrolyze the product, *i. e.*, to combine with the carbon dioxide formed by the elimination of the urea residue. Again, only barium benzenesulphonate was obtained, the guanidine residue being destroyed.

5. *Action of Potassium Carbonate.*—The material is boiled with an excess of potassium carbonate for four to five hours. Ammonia and carbon dioxide are evolved during the reaction. The resulting solution is evaporated to a small volume and, upon cooling, guanidine benzenesulphonate crystallizes out. The product was found to be identical with that obtained by hydrolyzing the sulphonate with hydrochloric acid. This experiment was carried out to determine whether guanidine carbonate is formed under the conditions described, but only the sulphonate was obtained, this being less soluble than the carbonate.

II. Paratoluenesulphonchloride and Urea.

1. *Preparation of Guanylurea p-Toluenesulphonate.*—The method of preparation is quite similar to that used in the preparation of the benzenesulphonate; 25 grams of *p*-toluenesulphonchloride and 18 grams of urea are ground together and brought into a thick-walled beaker of about 250 cc. capacity. The mixture is heated in the water-bath to 100°. The mass soon melts and separates into two distinct layers which are

---

[1] Ber. d. chem. Ges., 6, 1376.

mixed by stirring. After a few minutes the mass begins to react. Once begun, the reaction proceeds very rapidly and requires careful attention at this point. To secure a clean reaction the beaker should be kept well immersed in the bath and the contents vigorously stirred, best with a spatula. If left alone the reaction becomes violent and a hard, amorphous mass is obtained which is difficultly soluble in water and cannot be recrystallized. As soon as the mass has solidified it may safely be left to itself. The bath is kept at the boiling temperature and the contents of the beaker occasionally stirred till hydrochloric acid is no longer evolved. After the completion of the reaction, which usually requires from three to four hours, the mass should have the form of a white crystalline powder. The product thus obtained is allowed to cool and is then dissolved in 150 cc. boiling water. On standing, the sulphonate is deposited from the solution in colorless, wart-like aggregates, which can easily be purified by recrystallization from water. It cannot be distinguished in appearance from the benzenesulphonate. The guanylurea *p*-toluenesulphonate melts at 224° (uncorr.). The yield is approximately the same as that of the benzenesulphonate—60 to 70 per cent.

The analyses gave the following results:

I. 0.2151 gram substance gave 0.3114 gram CO_2 and 0.0988 gram H_2O.

II. 0.2178 gram substance gave 0.3158 gram CO_2 and 0.103 gram H_2O.

III. 0.1668 gram substance gave 0.144 gram $BaSO_4$.

IV. 0.159 gram substance gave 0.1365 gram $BaSO_4$.

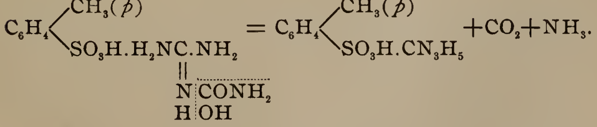
V. 0.2063 gram substance gave 35.8 cc. N at 13° and 757 mm. pressure.

VI. 0.2003 gram substance gave 36.1 cc. N at 20° and 755 mm. pressure.

	Calculated for $C_9H_{14}SN_4O_4$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	39.42	39.48	39.54	....	....	....	....
H	5.11	5.13	5.29	....	....	....	....
S	11.68	....	....	11.86	11.76	....	....
N	20.44	....	....	....	....	20.42	20.52

Prepared by the method just described, the sulphonate crystallizes in warts, unless allowed to separate from a very dilute solution by spontaneous evaporation. Under these conditions it may be obtained in colorless plates. It can be heated to 150° in the air without change, but above this temperature it slowly decomposes. The salt was also prepared by bringing together guanylurea and *p*-toluenesulphonic acid. It crystallized in plates, which had the same melting-point as the wart form, 224°.

2. *Action of Hydrochloric Acid.*—Ten grams of the product are heated in a sealed tube to 170° to 180° for six hours with about 20 cc. of hydrochloric acid (1 part of concentrated hydrochloric acid to 3 parts of water). Strong pressure is developed during the action and carbon dioxide escapes when the tube is opened. The resulting product is dissolved in a small quantity of hot water and the solution allowed to cool. Guanidine *p*-toluenesulphonate crystallizes out in delicate leaflets or large, colorless plates, depending on the concentration of the solution. The salt is purified by recrystallization from water and then has the melting-point 206°. The sulphonate was also made by bringing together guanidine carbonate and *p*-toluenesulphonic acid. The product thus obtained was compared with the sulphonate made as described above and the two were found to be identical. The salt is easily soluble in hot, tolerably difficultly soluble in cold, water. The reaction with hydrochloric acid may be represented by the following equation:



$$C_6H_4\left<\begin{matrix}CH_3(p)\\ SO_3H.H_2NC.NH_2\\ \qquad\qquad\ \ \| \\ \qquad\qquad\ \ N\,\vdots\,CONH_2 \\ \qquad\qquad\ \ H\,\vdots\,OH\end{matrix}\right. = C_6H_4\left<\begin{matrix}CH_3(p)\\ SO_3H.CN_3H_5\end{matrix}\right. + CO_2 + NH_3.$$

Analyses gave the following results: III, IV, and VII were obtained from the product of hydrolysis, and I, II, V, and VI from the synthetically prepared product.

I. 1758 gram substance gave 27.6 cc. N at 20° C. and 767 mm. pressure.

II. 0.1873 gram substance gave 30.2 cc. N at 24° and 763.4 mm. pressure.

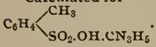
III. 0.1929 gram substance gave 30.8 cc. N at 24° and 774 mm. pressure.

IV. 0.1615 gram substance gave 26.5 cc. N at 27° and 764 mm. pressure.

V. 0.1649 gram substance gave 0.165 gram $BaSO_4$.

VI. 0.1671 gram substance gave 0.1695 gram $BaSO_4$.

VII. 0.1743 gram substance gave 0.1772 gram $BaSO_4$.

	Calculated for  $C_6H_4\left\langle\begin{matrix}CH_3\\SO_2.OH.CN_3H_5\end{matrix}\right.$.	Found.						
		I.	II.	III.	IV.	V.	VI.	VII.
N	18.18	18.14	18.16	18.25	18.19	....	....	....
S	13.85	....	....	....	....	13.75	13.93	13.96

3. *Action of Nitric Acid.*—To 10 grams of the product, 20 cc. of fuming nitric acid (sp. gr. 1.5) are cautiously added in small portions. The reaction is quite violent and the material passes into solution with copious evolution of dense fumes. The heat of reaction is sufficient to produce boiling. The solution is kept at the boiling-point by gently heating until there is no further evidence of action. The solution is then evaporated on the water-bath till the excess of nitric acid is expelled. The residue thus obtained forms a viscous mass having a deep-yellow color, and, on cooling, solidifies. This mass is dissolved in a small volume of hot water and, upon cooling, nitroguanidine separates out in the characteristic asbestos-like mass of fine needles. The product thus obtained is identical with that obtained from guanylurea benzenesulphonate.

Under the conditions of the reaction, the formation of one or more mononitrosulphonic acids is to be expected. By neutralizing the mother-liquor from the nitroguanidine with barium hydroxide a difficultly soluble salt is obtained. It crystallized in small plates of a pearly luster.

Analyses gave the following results :

I. 0.2942 gram anhydrous salt gave 0.1202 gram $BaSO_4$.
II. 0.2549 gram anhydrous salt gave 0.1047 gram $BaSO_4$.
III. 0.313 gram salt lost 0.0188 gram H_2O at 12°.
IV. 0.2712 gram salt lost 0.0163 gram H_2O at 12°.

	Calculated for $\left(C_6H_3(NO_2)\begin{smallmatrix}CH_3\\SO_3\end{smallmatrix}\right)_2Ba + 2H_2O$.	Found. I.	II.	III.	IV.
Ba	22.64	22.58	22.7	....	....
H_2O	5.95	....	....	6.0	6.01

This salt is probably derived from the acid of the formula $C_6H_3\begin{cases}CH_3\\NO_2(m)\\SO_3H(p)\end{cases}$. It has been described by Beilstein and Kuhlberg.[1]

4. *Urea and Paratoluenesulphonchloride in Alcoholic Solution.*—Twenty-five grams of *p*-toluenesulphonchloride are dissolved in the smallest possible quantity of alcohol, and to this solution is added a solution of 12 grams of urea in alcohol. The mixture is allowed to stand for several hours and then evaporated to a small volume. The product thus obtained is recrystallized from water. From a dilute aqueous solution it can be obtained in beautiful interlocked plates several centimeters in length. When pure it melts at 178° C.

Analyses gave the following results :

I. 0.2024 gram substance gave 0.3085 gram CO_2 and 0.0984 gram H_2O.

II. 0.2124 gram substance gave 0.3253 gram CO_2 and 0.1025 gram H_2O.

III. 0.2428 gram substance gave 0.3711 gram CO_2 and 0.117 gram H_2O.

IV. 0.1976 gram substance gave 20.4 cc. N at 19°.5 and 758 mm. pressure.

V. 0.2017 gram substance gave 20.63 cc. N at 18° and 764 mm. pressure.

VI. 0.203 gram substance gave 0.2096 gram $BaSO_4$.

	Calculated for $C_8H_{12}SN_2O_4$.	Found. I.	II.	III.	IV.	V.	VI.
C	41.61	41.59	41.8	41.71	....	....	....
H	5.21	5.33	5.39	5.39	....	....	....
N	12.14	....	....	....	12.16	12.14	....
S	13.87	....	....	....	....	....	14.14

---

[1] Ann. Chem. (Liebig), 155, 18.

As is shown by the above analyses, the product contains the elements of one molecule of water more than is required by the formula for the simple ureid. As this water cannot be expelled by heat it seemed probable that the sulphonchloride had been hydrolyzed and that the product really obtained is the sulphonate of urea. This view was confirmed by bringing together urea and free *p*-toluenesulphonic acid. The resulting product was found to be identical with that obtained from the chloride. The formation of the sulphonate is to be explained by the fact that the sulphonchloride reacts with the alcohol, giving the free sulphonic acid which at once combines with the urea. It is interesting to note that urea *p*-toluenesulphonate is quite difficultly soluble in water.

III. Orthotoluenesulphonchloride and Urea.

1. *Preparation of Guanylurea o-Toluenesulphonate.*—Twenty-five grams of the chloride and 18 grams of urea are brought together in a thick-walled beaker of suitable capacity and heated to 100° on the water-bath. The mass soon melts, forming two distinct layers which, upon stirring, soon begin to react. Constant and thorough stirring greatly facilitate the reaction, which usually requires six to eight hours' heating for completion. A marked difference in the ease with which the isomeric toluenesulphonchlorides react with urea is thus shown, the parachloride reacting much more readily than the ortho. When the mass has completely solidified and no more hydrochloric acid is evolved, it is allowed to cool and is then dissolved in a small quantity of hot water. The sulphonate crystallizes in the characteristic form of warts. It cannot be distinguished in appearance from the *p*-toluenesulphonate with which it is isomeric. It melts at 205° (uncorr.). Treated with sodium hydroxide and copper sulphate, the characteristic rose-red copper derivative of guanylurea is obtained. The results of the analyses follow:

I. 0.2378 gram substance gave 42.2 cc. N at 21°.5 and 765.5 mm. pressure.

II. 0.2352 gram substance gave 42.8 cc. N at 24° and 762 mm. pressure.

III. 0.1727 gram substance gave 0.1497 gram $BaSO_4$.

IV. 0.1856 gram substance gave 0.1578 gram $BaSO_4$.

	Calculated for $C_9H_4SN_4O_4$.	Found. I.	II.	III.	IV.
N	20.44	20.3	20.46	....	....
S	11.68	....	....	11.89	11.68

Guanylurea *o*-toluenesulphonate was also made by bringing together *o*-toluenesulphonic acid and guanylurea. Thus formed it crystallizes in colorless plates, melting at 205°.

2. *Action of Nitric Acid.*—To 10 grams of the sulphonate 20 cc. of fuming nitric acid (sp. gr. 1.50) are cautiously added. The reaction is quite violent and the material at once passes into solution with copious evolution of dense fumes. The heat of reaction is sufficient to set up boiling. The solution is maintained at the boiling-point by gently heating until there is no further evidence of action. The solution is then evaporated on the water-bath till the excess of nitric acid is expelled. The residue thus obtained forms a viscous mass of a deep-yellow color and solidifies upon cooling. The product is dissolved in a small quantity of boiling water and, upon cooling, nitroguanidine crystallizes out in the characteristic asbestos-like mass of fine needles. The mother-liquor was not examined for the nitrotoluenesulphonic acids.

IV. α-Naphthalenesulphonchloride and Urea.

1. *Preparation of Guanylurea α-Naphthalenesulphonate.*—Twenty grams of *α*-naphthalenesulphonchloride and 12 grams of urea are heated on the water-bath to 100°. The mixture soon melts, forming two distinct layers which are mixed by stirring. The resulting oil gradually thickens and finally solidifies. To insure a clean reaction the mixture must be thoroughly and constantly stirred. As soon as the mass has solidified it may safely be left to itself. The bath is kept at the boiling temperature until hydrochloric acid is no longer evolved. After cooling, the product is dissolved in boiling water. The sulphonate is deposited in the characteristic wart-like masses. It is markedly less soluble, both in cold and in hot water, than the sulphonates already described. With sodium hydroxide and copper sulphate it yields the characteristic copper derivative of guanylurea. The sulphonate melts at 223° C.

Analyses gave the following results:

I. 0.2422 gram substance gave 38.0 cc. N at 22° and 768.3 mm. pressure.

II. 0.2035 gram substance gave 32.05 cc. N at 21°.5 and 761 mm. pressure.

III. 0.379 gram substance gave 0.285 gram $BaSO_4$.

IV. 0.2348 gram substance gave 0.1796 gram $BaSO_4$.

	Calculated for $C_{12}H_{14}SN_4O_4$.	Found.			
		I.	II.	III.	IV.
N	18.06	17.98	17.95	....	....
S	10.32	....	....	10.33	10.5

The sulphonate was also prepared by bringing together the sulphonic acid and guanylurea. This synthesis is notable as being the only one in which the sulphonate was obtained in the wart-like form.

2. *Action of Hydrochloric Acid.*—Ten grams of the product are heated in a sealed tube for six hours at 150° with about 20 cc. of hydrochloric acid (1 part concentrated hydrochloric acid and 3 parts water). A higher temperature is to be avoided during the reaction since α-naphthalenesulphonic acid is unstable above 150°. The resulting product is crystallized from water. It is guanidine α-naphthalenesulphonate as was shown by preparing the salt from guanidine carbonate and the free sulphonic acid. From a dilute aqueous solution it crystallizes in large rosettes of colorless needles which are difficultly soluble in cold water. The salt has no definite melting-point, a fact which is probably due to the instability of α-naphthalenesulphonic acid at high temperatures.

V. β-Naphthalenesulphonchloride and Urea.

1. *Preparation of Guanylurea β-Naphthalenesulphonate.*—
—Twenty grams of β-naphthalenesulphonchloride and 12 grams of urea are heated together in a thick-walled beaker to 100° on the water-bath. The mass begins to melt at once and soon separates into two distinct layers, which are mixed by stirring. Once begun the reaction proceeds rapidly and requires close attention at this stage. The beaker should be kept well immersed in the water and the contents thoroughly stirred to secure a clean reaction. Unless these pre-

cautions are taken the reaction becomes violent and takes an entirely different course. Here, again, there is to be noted a marked difference in the ease with which α- and β-naphthalenesulphonchlorides react with urea. The β-sulphonchloride reacts much more readily than the α-sulphonchloride. The bath is kept at the boiling temperature and the contents of the beaker occasionally stirred until no more hydrochloric acid is evolved. After the completion of the reaction, which usually requires from three to four hours, the mass is allowed to cool and is then dissolved in hot water. The sulphonate is deposited in hard masses, consisting of very fine blades. It is purified by recrystallizing from water. It is notable as being the only sulphonate thus far studied which does not crystallize in the wart form when prepared from the sulphonchloride and urea, and as being the most difficultly soluble in water. Guanylurea β-naphthalenesulphonate melts at 237° (uncorr.). Treated with sodium hydroxide and a dilute solution of copper sulphate it yields the copper derivative of guanylurea.

The analyses gave the following results:

I. 0.197 gram substance gave 30.7 cc. N at 21° and 768 mm. pressure.

II. 0.2061 gram substance gave 31.4 cc. N at 17° and 769 mm. pressure.

III. 0.1718 gram substance gave 0.1306 gram $BaSO_4$.

IV. 0.2093 gram substance gave 0.1593 gram $BaSO_4$.

	Calculated for $C_{12}H_{14}SN_4O_4$.	Found. I.	II.	III.	IV.
N	18.06	17.94	17.9	....	....
S	10.32	....	....	10.44	10.46

The sulphonate was also made by bringing together the sulphonic acid and guanylurea, and this was found to be identical with that described above.

2. *Action of Hydrochloric Acid.*— Ten grams of the product are heated in a sealed tube at 160° for six hours with about 20 cc. of strong hydrochloric acid. Strong pressure is developed in the tube. The product obtained is guanidine α-naphthalenesulphonate. From a dilute solution it crystallizes in clusters of long colorless needles; from a concentrated solution in very fine needles or in fine blades. The sulphonate is difficultly

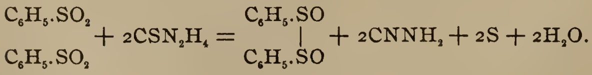
soluble in cold water. It melts at 259°. The salt was also prepared, for the purpose of comparison, by bringing together guanidine carbonate and β-naphthalenesulphonic acid. The two products were found to be identical.

The treatment of urea with an aromatic sulphonchloride is thus shown to furnish a convenient method for the preparation of guanylurea and also of guanidine, though the preparation of the latter by the method of Volhard[1] from ammonium sulphocyanate is probably somewhat more economical.

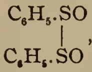
ON THE ACTION OF AROMATIC SULPHONCHLORIDES ON THIOUREA.

By Ira Remsen and H. J. Turner.

The interesting results obtained in studying the action of aromatic sulphonchlorides on urea, an account of which is given in the preceding article, led to the experiments described in this article. As will be seen, the action of the sulphonchlorides on thiourea is entirely different from that which takes place with urea itself. The reaction is somewhat complicated. In the first place the thiourea abstracts the chlorine from the sulphonchloride and forms with this chlorine the *dithiourea dichloride*, $(CSN_2H_4)_2Cl_2$, first obtained by Claus[2] by passing chlorine into a cold saturated aqueous or alcoholic solution of thiourea. The residues of the two molecules of the sulphonchloride then react with two more molecules of the thiourea. Reduction takes place with separation of sulphur and probably the formation of cyanamide. The reduction of the two residues of the sulphonchloride leads to the formation of a disulphoxide. For example, in the case of benzene sulphonchloride the reaction takes place as represented in the following equation :



$$\begin{array}{l} C_6H_5.SO_2 \\ C_6H_5.SO_2 \end{array} + 2CSN_2H_4 = \begin{array}{c} C_6H_5.SO \\ | \\ C_6H_5.SO \end{array} + 2CNNH_2 + 2S + 2H_2O.$$



The product represented by the formula $\begin{array}{c} C_6H_5.SO \\ | \\ C_6H_5.SO \end{array}$, is the *ben-*

---

[1] J. prakt. Chem. [2], 9, 15.

[2] Ann. Chem. (Liebig), 179, 139 (1875).

zene disulphoxide or *phenyl benzenethiosulphonate* of Otto.[1] As will be pointed out further on, Otto holds that this substance has the structure represented by the formula $C_6H_5.SO_2.SC_6H_5$,—that it is in fact the phenyl ester of benzenethiosulphonic acid. He obtained it by means of quite different reactions but we have established the identity of his product with ours.

In brief, then the changes that take place when benzenesulphonchloride and this urea are brought together in alcoholic solution are represented by the following two equations:

$$(1)\ 2C_6H_5.SO_2Cl + 2CSN_2H_4 = (C_6H_5SO_2)_2 + (CSN_2H_4)_2Cl_2;$$

$$(2)\ (C_6H_5SO_2)_2 + 2CSN_2H_4 = (C_6H_5SO)_2 + 2CNNH_2 + 2S + 2H_2O.$$

The reactions take place so smoothly that they furnish an excellent method for the preparation of the disulphoxide—apparently better than those made use of by Otto.

The action of paratoluenesulphonchloride on thiourea has also been studied and we have found that it takes place in general the same as that of benzenesulphonchloride on urea.

I. Benzenesulphonchloride and Thiourea.

When benzenesulphonchloride and urea in the dry condition are gently warmed together, reaction takes place when the temperature of 40° is reached. Heat is evolved, the mass suddenly turns yellow, sulphur separates, and hydrochloric acid is given off in quantity. The reactionis almost violent, and is complete in a few minutes. When cold, the mixture thus formed consists of a heavy, yellowish oil saturated with sulphur, crystals of sulphur, and a white, amorphous solid. Sometimes the reaction takes place slowly. This seems, however, to make no difference in the result.

The yellowish oil is soluble in carbon bisulphide, alcohol, acetic acid, and ether, but insoluble in water. It is not volatile with water wapor. It is saturated with sulphur which slowly crystallizes out. This oil could not be purified. When alcohol is used as a solvent the reaction takes place quietly with but little elevation of temperature. After the reaction is over fine needles separate, and the deposit is increased by the addition of ether. The crystals having been filtered off, water is added to the mother-liquor when a colorless oil is thrown down. This solidifies after a time. The needles first deposited proved to be dithiourea dichloride; the product that appears first as an oil, which then solidifies, proved to be benzene disulphoxide (or phenyl benzenethiosulphonate). The best method of procedure was found to be the following:

---

[1] Ann. Chem. (Liebig), **145**, 317 (1868).

Thiourea (4.6 grams) was dissolved in 150 cc. alcohol with the aid of heat, and benzenesulphonchloride (5 grams) added to this solution after it had cooled to the temperature of the room. The mixture became slightly warm. On cooling, fine crystals separated, and the quantity of the deposit was increased by the addition of 150 cc. ether. After two hours the crystals were filtered off, washed, at first with a mixture of alcohol and ether, then with ether, and finally dried on paper, and over sulphuric acid in a desiccator. The product thus prepared was found to be quite pure. If allowed to crystallize slowly from the alcoholic solution some change takes place in it. It then contains sulphur, from which it is impossible to separate it.

The alcohol-ether solution filtered from the crystals was treated with four times its volume of water. This caused the precipitation of the oil, above referred to. The supernatant liquid was decanted, and the oil washed with water. After removal of the water the oil was allowed to stand in a desiccator over sulphuric acid, and in about twelve hours it solidified. It was then purified by three crystallizations from ether, when it was found to melt sharply at 45°. This product is benzene disulphoxide. That its formation is not due to the action of the water was shown by rapidly evaporating by means of a blast of air a portion of the alcohol-ether solution when a semi-liquid mass was obtained in which small crystals were embedded. These melted at 45° when recrystallized from ether. A second portion of the alcohol-ether solution was allowed to evaporate slowly over sulphuric acid in a partial vacuum and in this case also the disulphoxide was obtained in crystals which, when crystallized from ether, melted at 45°.

When, however, the alcohol-ether solution from which the dithiourea dichloride and the benzene disulphoxide had been removed was evaporated on a water-bath, a dark, thick liquid containing sulphur and phenyl sulphydrate was obtained. The latter was detected by its odor and by the characteristic test. A small portion was heated in a test-tube in the open end of which was a strip of paper saturated with a solution of lead acetate, when the yellow coloration of lead mercaptide was obtained.

The yield of the dithiourea dichloride corresponds to about 90 per cent of the chlorine contained in the sulphonchloride. In one experiment 5 grams of the sulphonchloride gave 2.95 grams of the dichloride. In another 8.46 grams of the sulphonchloride gave 5.16 grams of the dichloride.

The yield of the disulphoxide corresponds to over 50 per cent of the phenyl contained in the sulphonchloride. This is 50 per cent better than by other methods hitherto employed. In one experiment 5 grams of the sulphonchloride gave 1.91 grams of the disulphoxide. In another 200 grams of the sulphonchloride gave 83 grams of the disulphoxide in the crystallized condition.

Dithiourea Dichloride.—This substance is soluble in water and alcohol, from which it can be crystallized only with difficulty, and when thus obtained, it always contains sulphur. From hydrochloric acid it can be easily obtained in transparent needles. It is insoluble in ether. It decomposes at 80° C. Alcohol and water decompose it slowly, alkalies rapidly, into hydrochloric acid, sulphourea, and cyanamide, with the separation of one-half its sulphur, as the following figures show:

1.9572 dithiocarbamide dichloride gave 0.2760 gram sulphur, or 14.12 per cent. The sulphur calculated for $(CSN_2H_4)_2Cl_2$ is 28.72 per cent., one-half of which is 14.36 per cent.

The analyses gave the following results:

I. 0.5761 gram substance gave 0.7336 gram AgCl (31.63 per cent Cl) and 1.1949 grams $BaSO_4$ (28.48 per cent S).

II. 0.1789 gram substance gave 0.2293 gram AgCl (31.84 per cent Cl) and 0.3727 gram $BaSO_4$ (28.61 per cent S).

III. 0.1885 gram substance gave 0.0739 gram CO_2 (10.69 per cent C) and 0.0606 gram H_2O (3.58 per cent H).

	Calculated for $(CSN_2H_4)_2Cl_2$.	Found. I.	II.
C	10.77	10.60	....
H	3.55	3.58	....
S	28.72	28.48	28.61
Cl	31.78	31.63	31.84

Claus[1] first prepared dithiourea dichloride by passing dry chlorine into a cold saturated aqueous or alcoholic solution of sulphourea :

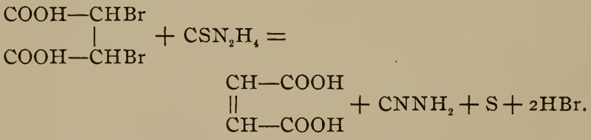
$$2CSN_2H_4 + 2Cl = (CSN_2H_4)_2Cl_2.$$

McGowan[2] prepared it by the action of trichlormethylsulphonchloride on sulphourea :

$$4CSN_2H_4 + 2CCl_3SO_2Cl = (CSN_2H_4)_2Cl_2 + CSN_2H_3.CCl_3SO_2 + CSN_2H_4.CCl_3SO_2H.$$

Under similar conditions methylsulphon- and dichlormethylsulphonchlorides, CH_3SO_2Cl and $CCl_2H.SO_2Cl$, yield the same product, as does also phosphorus oxychloride.

Dibromsuccinic acid was converted by Nencki and Sieber[3] into fumaric acid by boiling with it sulphourea, under which conditions, not the dibromide, but its decomposition-products were obtained, thus :



$$\begin{array}{l} COOH—CHBr \\ \quad\quad\ | \\ COOH—CHBr \end{array} + CSN_2H_4 = \begin{array}{l} CH—COOH \\ \| \\ CH—COOH \end{array} + CNNH_2 + S + 2HBr.$$

While the sulphonchlorides add chlorine to sulphourea easily, the chlorine acting like free chlorine, the chlorides of carboxyl acids do not.

With benzoyl chloride and sulphourea, Pike[4] obtained benzoyl thiocarbamide,

$$C_6H_5.COCl + CSN_2H_4 = C_6H_5CO.CSN_2H_3 + HCl.$$

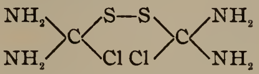
With acetyl chloride Claus[5] obtained an addition-product, thus :

---

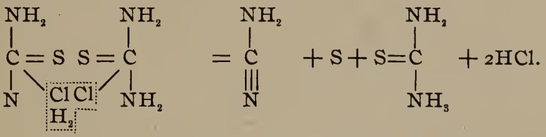
[1] Ann. Chem. (Liebig), **179**, 139 (1875).
[2] J. Chem. Soc., **49**, 191 (1896).
[3] J. prakt. Chem., **25**, 79 (1882).
[4] Ber. d. chem. Ges., **6**, 725 (1873).
[5] *Ibid.*, **8**, 41 (1875).

$$CSN_2H_4 + CH_3COCl = CSN_2H_4.CH_3COCl.$$

The percentage composition found by analysis agrees as well, of course, for a monosubstitution-product, CSN_2H_3Cl, as for a diaddition-product, $(CSN_2H_4)_2Cl_2$. The very curious decomposition of the substance by water into cyanamide, sulphourea, sulphur, and hydrochloric acid led Claus[1] to consider the substance a dichloride of dithiocarbamide, whose structure is represented thus:



and its decomposition by the equation:



From the ease with which the sulphur separates, the two sulphourea molecules are believed to be united through sulphur. The sulphur is doubly linked to carbon in sulphourea. By breaking this double bond, it becomes possible for the sulphur to unite with the sulphur of a second molecule, forming a dithiourea, which would be an unsaturated compound, capable of taking up two halogen atoms.

As will be shown farther on, the behavior of the dichloride towards potassium benzenesulphinate is strictly analogous to the action of dihalogen addition-products of certain unsaturated hydrocarbons, for example, stilbene dibromide,

$$C_6H_5CHCl = ClHC.C_6H_5,$$

toward the sulphinate. The dichloride behaves fully in accord with the formula of Claus.

This tendency of sulphourea to polymerize, to form an unsaturated dithiocarbamide, seems to explain why it acts differently from ordinary urea toward the sulphonchlorides. The molecule of sulphourea itself is not double; it corresponds to the single formula, as is shown by the following determination of its molecular weight by the freezing-point method:

---

[1] Ann. Chem. (Liebig), 179, 139 (1875).

	I.	II.	III.
Weight of substance	2.3145	1.7584	3.4861
Weight of water	54.0029	46.0813	54.0029
Freezing-point lowering	1.029° C.	0.872°	1.295°

	Calculated.	Found.		
		I.	II.	III.
Molecular weight	76	78.3	82.3	79.4

Benzene Disulphoxide.—Benzene disulphoxide, or phenyl ester of benzenethiosulphonic acid, is a colorless transparent solid, melting at 45° C.; very soluble in ether and benzene, less in alcohol, and insoluble in water. By evaporation of its ether solution it is obtained in large prisms, one of which was 2.5 cm. in length.

The analyses gave the following results:

I. 0.1407 gram substance gave 0.2960 gram CO_2 (57.38 per cent C), and 0.0496 gram H_2O (3.92 per cent H).

II. 0.2137 gram substance gave 0.4501 gram CO_2 (57.44 per cent C) and 0.0806 gram H_2O (4.19 per cent H).

III. 0.1997 gram substance gave 0.3759 gram $BaSO_4$ (26.24 per cent S).

IV. 0.1318 gram substance gave 0.2439 gram $BaSO_4$ (25.41 per cent S).

	Calculated for $C_{12}H_{10}S_2O_2$.	Found.	
		I.	II.
C	57.6	57.38	57.44
H	4.0	3.92	4.19
S	25.6	26.24	25.41

The molecular weight of the disulphoxide was determined by the freezing-point method with benzene as the solvent. The results show that the molecular weight is correctly represented by the formula $C_{12}H_{10}S_2O_2$.

The figures follow:

	I.	II.
Weight of substance	2.8421	4.1104
Weight of benzene	47.7407	47.7407
Freezing-point lowering	1.145° C.	1.640°

	Calculated for $C_{12}H_{10}S_2O_2$.	Found.	
		I.	II.
Molecular weight	250	254.7	257.2

The disulphoxide was saponified by potassium hydroxide to potassium benzenesulphinate and phenyl disulphide according to the equation

$$3C_{12}H_{10}SO_2 + 4KOH = 4C_6H_5SO_2K + (C_6H_5)_2S_2 + 2H_2O.$$

Five grams substance were dissolved in 50 cc. alcohol, 3 grams potassium hydroxide added, and the whole boiled with return condenser on a water-bath for one hour. When cooled the reaction mixture consisted of a solid cake and a liquid. The solid was redissolved in hot alcohol from which it crystallized in thin needles, melting at 60° C. A small portion was reduced by zinc and hydrochloric acid, yielding the characteristic phenyl sulphydrate. The solid was phenyl disulphide, $(C_6H_5)_2S_2$. The liquid portion was evaporated to dryness, and the residue extracted with alcohol. This was evaporated, dissolved in a little water, and dilute sulphuric acid added, when, upon cooling, benzenesulphinic acid crystallized out which melted at 83° C. The identification of the benzene disulphoxide with that prepared by Otto was complete.

II. Paratoluenesulphonchloride and Sulphourea.

Ten grams of *p*-toluenesulphonchloride were dissolved in 300 cc. alcohol and added to 8 grams sulphourea dissolved in alcohol; this was in the proportion of 1 molecule of chloride to 2 of sulphourea. 500 cc. ether were added to cause the separation of the dithiourea dichloride, which was filtered off, washed, and dried. The *p*-toluene disulphoxide was then precipitated by adding three volumes of water, separated by decantation, washed, and allowed to stand over night, when it solidified. When recrystallized twice from ether] *p*-toluene disulphoxide melted at 78° C.

Paratoluene Disulphoxide.—This, like benzene disulphoxide, is soluble in ether, benzene, and alcohol, insoluble in water. When first precipitated it forms a colorless oil, solidifying slowly. It crystallizes in prisms, melting-point 78° C.

Analyses gave the following results :

I. 0.2304 gram substance gave 0.5096 gram CO_2 (60.32 per cent C) and 0.1062 gram H_2O (5.04 per cent H).

II. 0.1922 gram substance gave 0.3248 gram $BaSO_4$ (23.20 per cent S).

III. 0.2376 gram substance gave 0.3957 gram $BaSO_4$ (22.87 per cent S).

	Calculated for $C_{14}H_{14}S_2O_2$.	Found. I.	II.
C	60.43	60.32	....
H	5.04	4.12	....
S	23.02	23.20	22.87

The molecular weight was determined by the freezing-point method and it was found to be that corresponding to the formula $C_{14}H_{14}S_2O_2$. The figures obtained follow :

	I.	II.
Weight of benzene	43.5906	43.5906
Weight of substance	2.4622	3.9117
Freezing-point lowering	1.021°	1.541°

	Calculated for $C_{14}H_{14}S_2O_2$.	Found. I.	II.
Molecular weight	278	282.6	285.3

The disulphoxide was also saponified by potassium hydroxide, yielding tolyl disulphide, $(C_7H_7)_2S_2$, which melted at 41°, and potassium *p*-toluenesulphinate, from which was obtained the sulphinic acid melting at 80°. The reaction takes place according to the equation

$$3C_{14}H_{14}S_2O_2 + 4KOH = 4C_7H_7SO_2K + (C_7H_7)_2S_2 + 2H_2O.$$

No doubt remained that the substance was the *p*-toluenedisulphoxide of Otto.

III. Ammonium Sulphocyanate and Benzenesulphonchloride.

Ammonium sulphocyanate and benzenesulphonchloride were brought together in alcohol to ascertain if the sulphocyanate would act like its isomer, sulphourea.

Ten grams benzenesulphonchloride (1 molecule) were brought together with 8.5 grams ammonium sulphocyanate (2 molecules) in alcohol. Reaction was started on the water-bath, when a golden-yellow powder was precipitated. It was very slightly soluble in alcohol, insoluble in water, ether, and benzene. It did not melt at 230° C. Yield 8.3 grams. No disulphoxide, however, was precipitated upon addition of water to filtrate. On account of the complex nature of the sulphocyanic acid derivatives and the impossibility of obtaining the above substance in crystalline form, it was not further studied.

IV. Dithiocarbamide Dichloride and Salts of Sulphinic Acids.

As sulphourea and benzenesulphonchloride give benzene disulphoxide, it appeared possible that potassium sulphinate and dithiourea dichloride might give the same compound. If the former react according to the equation

$$2C_6H_5SO_2Cl + 4CSN_2H_4 = (CSN_2H_4)_2Cl_2 + [(C_6H_5SO_2)_2(CSN_2H_4)_2],$$

the latter might react thus:

$$(CSN_2H_4)_2Cl_2 + 2C_6H_5SO_2K = 2KCl + [(C_6H_5SO_2)_2(CSN_2H_4)_2].$$

According to this equation the disulphoxide is formed from the intermediate compound $[(C_6H_5SO_2)_2(CSN_2H_4)_2]$, which may be called dithiourea dibenzenesulphinate. Whether this intermediate compound is formed or not, benzene disulphoxide is formed as a product of the action of dithiourea dichloride on potassium benzenesulphinate.

Ten grams of potassium benzenesulphinate were dissolved in absolute alcohol and added to a cold concentrated alcoholic solution of 6.3 grams of dithiocarbamide dichloride. The potassium chloride was filtered off, dried, and weighed ; yield, 3.8 grams. Water was added to the filtrate to precipitate the disulphoxide. It came down as a colorless oil and was treated in the usual way as described above, when it was obtained well crystallized, melting at 45° C. The yield was 6.94 grams, containing 51.9 per cent of the total phenyl of the acid chloride. Upon evaporation, the mother-liquor yielded sulphur and a sulphydrate. When the substances were brought together in water instead of alcohol, the mixture at once turned white from the drops of oil held in suspension, which, upon settling to the bottom of the vessel, left the supernatant liquid clear. After twelve hours the oil, which had now solidified, was washed with water and treated with ether, in which it was not completely soluble. From the ether solution benzene-disulphoxide was obtained melting at 45° C. The residue insoluble in ether was soluble in hot alcohol, from which a substance crystallized in fine white crystals. This melted at 99°.5 and was found to be free of nitrogen. The quantity of the substance was too small to permit of an analysis. Upon platinum foil it burned, showing it to be organic.

The *p*-toluene disulphoxide was prepared in a similar way. Here, too, was obtained a small quantity of a white substance crystallizing from alcohol in needles, melting at 155° to 158° C. It was likewise free of nitrogen.

Märcker[1] was the first to prepare *p*-toluene disulphoxide. He made it by oxidizing benzyl sulphydrate with nitric acid, and he gave it the name oxybenzyl disulphide. The reaction is expressed by the equation

$$2C_7H_7.SH + 3O = C_{14}H_{14}S_2O_2 + H_2O.$$

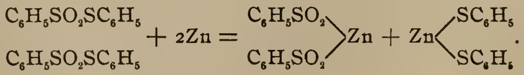
Otto[2] was the next to prepare the substance, and he first prepared the homologous phenyl compound. He obtained the compounds by heating the corresponding sulphinic acids at 120° in closed tubes. Benzenesulphinic acid yields benzene disulphoxide and sulphonic acid,

$$3C_6H_5SO_2H = C_{12}H_{10}S_2O_2 + C_6H_5SO_3H + H_2O.$$

Otto and Pauly[3] obtained the disulphoxide from the sulphinates of the alkalies by the action of dehydrating agents, as sulphuric acid and phosphorus pentoxide. With potassium benzenesulphinate the reaction takes place as represented in the equation

$$3C_6H_5SO_2K + H_2SO_4 = C_{12}H_{10}S_2O_2 + C_6H_5SO_3K + K_2SO_4 + H_2O.$$

Otto[4] treated the compounds with zinc and thus obtained zinc mercaptide and zinc sulphinates, and for this reason he considered the so-called disulphoxides to be thioesters. Benzene disulphoxide is accordingly the phenyl ester of benzenethiosulphonic acid. The action of zinc is represented thus:



$$\begin{array}{l} C_6H_5SO_2SC_6H_5 \\ C_6H_5SO_2SC_6H_5 \end{array} + 2Zn = \left.\begin{array}{l} C_6H_5SO_2 \\ C_6H_5SO_2 \end{array}\right\rangle Zn + Zn\left\langle\begin{array}{l} SC_6H_5 \\ SC_6H_5 \end{array}\right. .$$

---

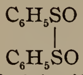
[1] Ann. Chem. (Liebig), **136**, 75 (1865).

[2] *Ibid.*, **145**, 10, 317 (1868).

[3] Ber. d. chem. Ges., **9**, 1640 (1876).

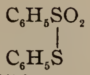
[4] *Ibid.*, **10**, 2181 (1877).

The disulphoxide differs from the thioester in the position of one oxygen atom, thus:



$$\begin{array}{c} C_6H_5SO \\ | \\ C_6H_5SO \end{array}$$

Disulphoxide.



$$\begin{array}{c} C_6H_5SO_2 \\ | \\ C_6H_5S \end{array}$$

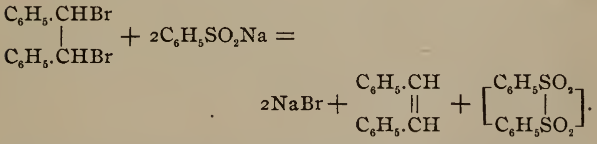
Thioester.

The first contains tetravalent sulphur; the latter a hexavalent sulphur atom, united with oxygen, and a bivalent sulphur atom not united with oxygen. Otto did not, however, succeed in effecting the synthesis of the compound by methods applicable to the preparation of the aliphatic thioesters. In his latest article (1896) he uses the term disulphoxide with thioester in parenthesis.

Escales[1] found that the disulphoxide is formed when phenylhydrazine reacts with benzenesulphinic acid to form benzenesulphonphenylhydrazide, thus:

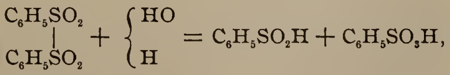
$$3C_6H_5SO_2H + C_6H_5HN.NH_2 = C_6H_5.HN.NH.SO_2C_6H_5 + C_{12}H_{10}S_2O_2 + H_2O.$$

The disulphoxide was also obtained by Otto[2] by the action of stilbene dibromide on sodium benzenesulphinate, when sodium bromide, stilbene (diphenylethylene) and a peculiar disulphone were formed:



$$\begin{array}{c} C_6H_5.CHBr \\ | \\ C_6H_5.CHBr \end{array} + 2C_6H_5SO_2Na = 2NaBr + \begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array} + \left[\begin{array}{c} C_6H_5SO_2 \\ | \\ C_6H_5SO_2 \end{array}\right].$$

The latter is incapable of existence in the presence of water, with which it forms sulphinic and sulphonic acids,



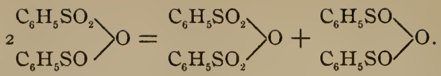
$$\begin{array}{c} C_6H_5SO_2 \\ | \\ C_6H_5SO_2 \end{array} + \left\{\begin{array}{l} HO \\ \\ H \end{array}\right. = C_6H_5SO_2H + C_6H_5SO_3H,$$

so that it may be regarded as a double anhydride of sulphinic and sulphonic acids, which yields the anhydrides of these two acids.

---

[1] Ber. d. chem. Ges., **18**, 1893 (1883).

[2] J. prakt. Chem., **53**, 1 (1896).



$$2\,\begin{matrix}C_6H_5SO_2\\ C_6H_5SO\end{matrix}\!>O = \begin{matrix}C_6H_5SO_2\\ C_6H_5SO_2\end{matrix}\!>O + \begin{matrix}C_6H_5SO\\ C_6H_5SO\end{matrix}\!>O.$$

Then the sulphinic acid changes, especially under pressure, into sulphonic acid and disulphoxide,

$$3C_6H_5SO_2H = C_6H_5SO_3H + C_{12}H_{10}S_2O_2.$$

In stilbene dibromide the two halogens are linked to different carbon atoms; if the two halogen atoms are linked to the same carbon atom, the disulphoxide is not obtained, but a sulphone.

Thus, with benzal chloride Otto[1] obtained chlorbenzylidenephenylsulphone,

$$C_6H_5.CHCl + C_6H_5SO_2Na = C_6H_5CHCl.SO_2.C_6H_5 + NaCl.$$

The action of dithiourea dichloride with benzenesulphinate is similar to that of stilbene dibromide with the sulphinate. In both cases the disulphoxide is formed.

ON THE ACTION OF THE CHLORIDES OF ORTHOSULPHOBENZOIC AND OF PARANITROORTHOSULPHOBENZOIC ACIDS ON UREA.

By Willis B. Holmes.

It was thought that the two isomeric chlorides of orthosulphobenzoic acid and the corresponding chlorides of paranitroorthosulphobenzoic acid might react with urea in different ways. This was found not to be the case. The two isomeric chlorides both gave the same products, and these proved to be quite different in character from those obtained when a simple aromatic sulphonchloride is allowed to act upon urea (see the two preceding articles).

Chlorides of Orthosulphobenzoic Acid. — Some changes have been made in the method adopted in passing from benzoic sulphinide to these chlorides. A brief account of the improved method follows: Two hundred grams of the purest commercial sulphinide[2] (saccharin) are placed in a large evaporating dish with 3 liters of water and 250 cc. of ordinary dilute hydrochloric acid. This mixture is then boiled for five or six hours, the volume being kept nearly constant until the sweet taste of the saccharin has entirely disappeared. It is then evaporated to about a liter, allowed to cool, filtered, and evaporated to dryness. The acid ammonium salt of orthosulphobenzoic acid thus obtained is washed with alcohol until perfectly white. It is then dissolved in enough water so that the hot solution is about half saturated, allowed to cool, and a little more than the required amount (2 molecules) of potassium hydroxide added. When cold, the addition of hydrochloric acid precipitates the acid potassium salt of orthosulphobenzoic acid in white plates. From the filtrate on evaporation more of the acid potassium salt can be obtained.

---

[1] J. prakt. Chem., 148, 517 (1889).

[2] I take pleasure in thanking the firm, Von Heyden, Radebeul, Germany, for sending me an abundant supply of the pure sulphinide.—I. R.

Fifty grams of the dried acid potassium salt are placed in a large mortar with 2.5 molecules of phosphorus pentachloride and the mixture intimately ground until reaction ensues. The resulting oil is then transferred to an evaporating dish, and placed on a steam-bath for several hours, until most of the phosphorus oxychloride has distilled off. It is then poured into a large bottle containing ice-water and shaken vigorously. After shaking with several changes of water it is ready for further use.

To obtain a mixture of the dry chlorides the oil is placed in a mortar with cracked ice and ground until it becomes solid. It is then filtered, washed with ice-water, and pressed between drying-paper, care being taken not to touch the product or have anything warm near it as the mixture melts at 21°. It is then dried in a desiccator in a cool place. One hundred grams of the mixed chlorides contain about 60 grams of the unsymmetrical chloride.

To obtain the symmetrical chloride the oil is at once dissolved in ether and transferred to a large separating funnel containing ice and water. Ammonia is then added, until after shaking for a few minutes the presence of ammonia is still detected. Hydrochloric acid is then added to neutralize the free ammonia, the ethereal solution washed, separated, and dehydrated with calcium chloride. On evaporating off the ether the chloride is obtained. This can be obtained perfectly pure by crystallizing from pure ligroin (b. p. 90° to 125°).

The product melting at 21°, formerly considered to be the unsymmetrical chloride, has been shown to be a mixture of the two chlorides.[1] The pure unsymmetrical chloride melts at 40° and is prepared as follows: The neutral potassium salt of orthosulphobenzoic acid obtained by neutralizing the acid potassium salt with potassium hydroxide is heated in a sealed tube for four hours with 1.5 molecules of phosphorus oxychloride at 135°. The product is transferred to a mortar, ground up with several changes of ice-water, filtered, dried, and crystallized from pure ligroin. The yield is about 50 per cent.

A mixture of these chlorides has the property of crystallizing apparently as a chemical individual. It crystallizes in long radiating tufts, which melt at 21°, and is not changed by further crystallization.[2]

Chlorides of Paranitroorthosulphobenzoic Acid.—The symmetrical chloride of paranitroorthosulphobenzoic acid was prepared as described by Henderson.[3]

In the preparation of the unsymmetrical chloride, the method of Hollis[4] was not followed. A much better method of preparation was as follows: The neutral potassium salt of paranitroorthosulphobenzoic acid is heated with 1.5 molecules of phosphorus oxychloride in a sealed tube for four hours at 135°. The product is then transferred to a mortar, ground up with several changes of ice-water, filtered, dried, and recrystallized from pure ligroin. Only the unsymmetrical chloride was obtained and was identical with that described by Hollis. The reaction is a very clean one with a uniform yield of 50 per cent.

Action of Urea on the Chlorides of Orthosulphobenzoic Acid.

Action on the Symmetrical Chloride.—A mixture of the symmetrical chloride with urea in the proportion of 1 molecule of the former to 4 of the latter, was heated in a test-tube at various temperatures. When heated over a free flame or above the melting-point of urea, violent reaction took place with a considerable evolution of heat. Hydrochloric acid was given off and biuret was formed. As the heat of the reaction was sufficient to destroy any excess of urea, no attempt was made to isolate the products.

---

[1] Ber. d. chem. Ges., 11, 1653 (1898).

[2] When certain investigations, now in progress in this laboratory, are completed, I shall have something further to say on this subject.—I. R.

[3] This JOURNAL, 25, 1.

[4] *Ibid.*, 23, 233.

When the mixture was heated at 100° the reaction proceeded very slowly and quietly without the evolution of heat. A mixture of the chloride and urea, in the proportion of 1 molecule to 4, was heated for several days at 100° in a test-tube. At first the mixture became liquid, forming two distinct layers. Stirring greatly facilitated the reaction. In the course of a few hours the mixture became pasty and stirring was necessary in order to insure a thorough mingling of the two constituents. At the end of two days the mass became hard. A little hydrochloric acid was given off during the experiment.

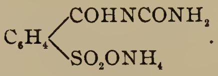
The hard cake formed was then dissolved in hot water. On cooling, a small quantity of a substance separated that was soluble in hot, but sparingly soluble in cold, water. This body contained no sulphur and appeared to be biuret. The mother-liquor, on concentration, yielded a very beautiful crystalline substance and small quantities of ammonium chloride. This substance had a strong crystallizing power and usually appeared in long, colorless, monoclinic prisms. It melted at 266°, was moderately soluble in water, but insoluble in alcohol or ether. It acted like an ammonium salt, giving off ammonia in the cold with weak alkalies. The yield was about 55 per cent of the theoretical and no other product was obtained.

Action on the Unsymmetrical Chloride.—The same method of procedure was followed with the unsymmetrical chloride. The chloride with urea in the proportion of 1 molecule to 4 was heated in a test-tube at 100° for several days. Reaction took place much more quickly than with the symmetrical chloride. The resulting product was dissolved in hot water. On cooling, a small quantity of a substance separated that was soluble in hot, but sparingly soluble in cold, water. This body contained no sulphur and was identical with that obtained from the symmetrical chloride. From the mother-liquor, on evaporation, the same characteristic, monoclinic prisms crystallized out that were obtained from the symmetrical chloride, and a small quantity of ammonium chloride. This substance melted at 266°, was moderately soluble in water, insoluble in alcohol or ether. It gave off ammonia in the cold with weak alkalies and was identical with the product obtained from the symmetrical chloride. The yield was about 55 per cent of the theoretical. On analysis it was found to have the following composition :

$$C_6H_4SO_5C_2H_7N_3.$$

	Calculated.	Found.	
		I.	II.
C	36.75	36.61	36.70
H	4.22	4.29	4.28
S	12.27	12.31	12.38
N	16.14	16.34	16.10

It proved to be the *ammonium salt of benzoylureaorthosulphonic acid*,



$$C_6H_4\left\langle\begin{array}{l}COHNCONH_2\\SO_2ONH_4\end{array}\right. .$$

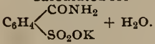
Action of Hydrochloric Acid.—On boiling with dilute hydrochloric acid the ammonium salt was hydrolyzed to the acid ammonium salt of orthosulphobenzoic acid. This, when treated with potassium hydroxide, gave off ammonia, and, when acidified with hydrochloric acid, it gave the characteristic acid potassium salt of orthosulphobenzoic acid.

Action of Potassium Hydroxide.—The ammonium salt was boiled with a dilute solution of potassium hydroxide for six hours. Ammonia was constantly given off, showing a slow hydrolysis. On evaporating the solution the potassium salt of orthobenzaminesulphonic acid separated out. This salt was very soluble in water and crystallized in monoclinic plates. It contained 1 molecule of water of crystallization and was identical with the potassium salt of orthobenzaminesulphonic acid described by Remsen and Karslake.[1] This showed that the urea residue was in the carbonyl group.

---

[1] This JOURNAL, 18, 826.

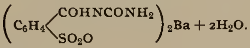
0.1339 gram substance gave 0.0096 gram H_2O.
0.1546 gram substance gave 0.0111 gram H_2O.
0.2099 gram substance gave 0.0769 gram K_2SO_4.
0.1386 gram substance gave 0.505 gram K_2SO_4.

	Calculated for  $C_6H_4\Big\langle\begin{matrix}CONH_2\\SO_2OK\end{matrix} + H_2O.$	Found.	
		I.	II.
H_2O	7.04	7.17	7.18
K	16.32	16.43	16.39

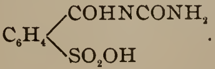
Action of Barium Hydroxide.—A solution of the ammonium salt was treated in the cold with an excess of barium hydroxide. Ammonia was given off, and after the solution had stood for some time the excess of barium hydroxide was removed by carbon dioxide. From the filtered solution, on evaporation, crystals of the barium salt of benzoylureaorthosulphonic acid separated out.

This salt was sparingly soluble in water and separated out in clusters of transparent, diamond-shaped crystals. It crystallized with 2 molecules of water of crystallization and effloresced on exposure to the air, becoming opaque.

0.3346 gram substance gave 0.0181 gram H_2O.
0.2109 gram substance gave 0.0110 gram H_2O.
0.1998 gram substance gave 0.0742 gram $BaSO_4$.
0.1972 gram substance gave 0.0732 gram $BaSO_4$.

	Calculated for  $\left(C_6H_4\Big\langle\begin{matrix}COHNCONH_2\\SO_2O\end{matrix}\right)_2Ba + 2H_2O.$	Found.	
		I.	II.
$2H_2O$	5.47	5.40	5.22
Ba	21.98	21.82	21.80

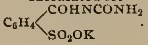
Benzoylureaorthosulphonic Acid.—The free acid was made by treating the barium salt with an equivalent amount of sulphuric acid. It is a strong acid, extremely soluble in water, separating out as a silky mass only when the solution is evaporated to a thick syrup. No attempt was made to analyze it, and from a study of its salts its composition proved to be that represented by the formula



$$C_6H_4\Big\langle\begin{matrix}COHNCONH_2\\SO_2OH\end{matrix}.$$

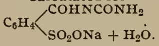
Potassium Salt.—This salt is moderately soluble in water, and separates out in especially well-defined, colorless, monoclinic prisms. It contains no water of crystallization and melts at 286°.

0.2406 gram substance gave 0.0740 gram K_2SO_4.
0.2465 gram substance gave 0.0753 gram K_2SO_4.

	Calculated for	Found.	
	 $C_6H_4\left\langle\begin{matrix}COHNCONH_2\\SO_2OK\end{matrix}\right.$.	I.	II.
K	13.85	13.80	13.71

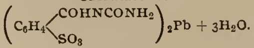
Sodium Salt.—This salt separates out in thick, opaque, poorly defined prisms, apparently of orthorhombic habit. It is quite soluble in water, contains 1 molecule of water of crystallization, and effloresces on exposure to the air.

0.6932 gram substance gave 0.0430 gram H_2O.
0.5936 gram substance gave 0.0369 gram H_2O.
0.1826 gram substance gave 0.0486 gram Na_2SO_4.
0.2274 gram substance gave 0.0606 gram Na_2SO_4.

	Calculated for	Found.	
	 $C_6H_4\left\langle\begin{matrix}COHNCONH_2\\SO_2ONa\end{matrix}\right. + H_2O$.	I.	II.
H_2O	6.33	6.20	6.22
Na	8.66	8.57	8.62

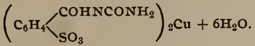
Lead Salt.—This salt is very soluble in water, separating out in clusters of thin, transparent, tabular plates. The crystals are not well defined, contain 3 molecules of water of crystallization, and effloresce on exposure to the air, becoming opaque.

0.5148 gram substance gave 0.0371 gram H_2O.
0.3417 gram substance gave 0.0254 gram H_2O.
0.1693 gram substance gave 0.0746 gram $PbSO_4$.
0.1742 gram substance gave 0.0770 gram $PbSO_4$.

	Calculated for	Found.	
	 $\left(C_6H_4\left\langle\begin{matrix}COHNCONH_2\\SO_3\end{matrix}\right.\right)_2Pb + 3H_2O$.	I.	II.
$3H_2O$	7.25	7.20	7.43
Pb	29.85	30.00	30.05

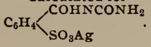
Copper Salt.—This salt is moderately soluble in water, crystallizes in clusters of long blue prisms, and contains 6 molecules of water of crystallization.

0.1957 gram substance gave 0.0324 gram H_2O.
0.2585 gram substance gave 0.0422 gram H_2O.
0.2010 gram substance gave 0.0292 gram CuO.
0.2161 gram substance gave 0.0315 gram CuO.

	Calculated for  $\left(C_6H_4\begin{array}{l}\diagup COHNCONH_2\\ \diagdown SO_3\end{array}\right)_2Cu + 6H_2O.$	Found. I.	 II.
$6H_2O$	16.45	16.60	16.33
Cu	11.52	11.59	11.62

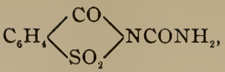
Silver Salt.—This salt was prepared by dissolving silver oxide in a solution of the free acid. It is moderately soluble in water, crystallizes in clusters of thick-pointed, poorly defined prisms, contains no water of crystallization, and darkens on exposure to the light.

0.2188 gram substance gave 0.0675 gram Ag.
0.2130 gram substance gave 0.0658 gram Ag.

	Calculated for  $C_6H_4\begin{array}{l}\diagup COHNCONH_2\\ \diagdown SO_3Ag\end{array}.$	Found. I.	 II.
Ag	30.74	30.85	30.90

Several explanations of the formation of the ammonium salt of benzoylureaorthosulphonic acid suggest themselves. It is a secondary product formed after the heated mass had been dissolved in water. The hydrochloric acid in the aqueous solution decomposed the original compound with the formation of ammonium chloride. All attempts to isolate the original product failed. The mass of chloride and urea, after heating, was extracted with ether and chloroform, but nothing was obtained. This probably disproves the theory that the chlorine atom of the carbonyl group was acted upon and the chlorine of the sulphonyl group removed by subsequent hydrolysis. It completely dissolved in alcohol, showing that the ammonium salt was not the original compound. On account of its extreme solubility in alcohol or water and of its poor crystallizing power, it was impossible to separate it from the large amount of urea present.

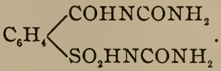
There are two possible theories to account for the formation of the ammonium salt. One molecule of urea may have reacted with one molecule of the chloride to form a ureid,



$$C_6H_4\left\langle\begin{array}{c}CO\\SO_2\end{array}\right\rangle NCONH_2,$$

which, on hydrolysis, would take up a molecule of water and give the free sulphonic acid. This, with the ammonium chloride formed from the decomposition of the urea hydrochloride, would give the ammonium salt.

On the other hand, two molecules of urea may have reacted with one molecule of the chloride to form a diureid,



$$C_6H_4\left\langle\begin{array}{l}COHNCONH_2\\SO_2HNCONH_2\end{array}\right. .$$

The urea residue in the sulphonyl group was then hydrolyzed to the ammonium salt. This latter view seems the more probable.

Action of Urea on the Chlorides of Paranitroorthosulphobenzoic Acid.

Action on the Symmetrical Chloride.—As a rule, the derivatives formed from the chlorides of paranitroorthosulphobenzoic acid are less soluble than the corresponding derivatives formed from the chlorides of orthosulphobenzoic acid. In view of this fact, the action of urea upon these chlorides was tried to see if some of the intermediate products of the reaction could not be isolated.

A mixture of the chloride and urea in the proportion of 1 molecule to 4 was heated at different temperatures. When heated over a free flame or above the melting-point of urea violent reaction took place. Hydrochloric acid was given off and there was a considerable evolution of heat. As the heat of the reaction was sufficient to destroy any excess of urea no attempt was made to isolate the products.

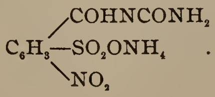
At 100° the reaction proceeded slowly and quietly without the evolution of heat. A mixture of the chloride and urea in the proportion of 1 molecule to 4, was heated for two days at 100°. At first the mass became liquid, forming two distinct layers. As the reaction proceeded stirring was necessary in order to insure a thorough mingling of the two constituents. Reaction took place more slowly than with the symmetrical chloride of orthosulphobenzoic acid.

The hard cake formed was dissolved in hot water. On cooling, a small quantity of a substance separated that was soluble in hot, but sparingly soluble in cold, water. It contained no sulphur and appeared to be biuret. The mother-liquor, on concentration, yielded small quantities of ammonium chloride and a well-crystallized substance of a pale-lemon color. This substance crystallized in diamond-shaped plates, and melted at 273°. It was moderately soluble in water, insoluble in alcohol or ether. It acted like an ammonium salt, giving off ammonia in the cold with weak alkalies. The yield was about 55 per cent and no other product was obtained.

Action on the Unsymmetrical Chloride.—The same method of procedure was followed with the unsymmetrical chloride. Reaction took place much more quickly than with the symmetrical chloride. The resulting product was dissolved in hot water. On cooling, a small quantity of a substance separated. This was soluble in hot, but sparingly soluble in cold, water. It was identical with that obtained from the symmetrical chloride and was probably biuret. From the mother-liquor, on evaporation, the same diamond-shaped plates separated that were obtained from the symmetrical chloride. These melted at 273°, were moderately soluble in water, insoluble in alcohol or ether. The substance gave off ammonia in the cold when treated with weak alkalies. It contained no water of crystallization and was identical with the product obtained from the symmetrical chloride. The yield was about 60 per cent. On analysis it gave the following results:

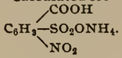
	Calculated for $C_8H_{10}O_7SN_4$.	Found. I.	II.
C	31.34	31.13	....
H	3.27	3.36	3.31
S	10.47	10.32	10.39
N	18.36	18.38	18.50

This substance proved to be the *ammonium salt of paranitrobenzoylureaorthosulphonic acid*,

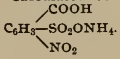


$$C_6H_3\begin{cases}COHNCONH_2\\SO_2ONH_4\\NO_2\end{cases}.$$

Action of Fuming Nitric Acid.—The salt was boiled with fuming nitric acid to see if any nitroguanidine was formed, as would be the case if one of the urea molecules had acted upon a urea residue. Nothing but the acid ammonium salt of paranitroorthosulphobenzoic acid was formed. This salt crystallized in monoclinic plates, and was very soluble in water. On treating a solution of this salt with potassium hydroxide, ammonia was given off and, on acidifying, the characteristic acid potassium salt of paranitroorthosulphobenzoic acid separated out.

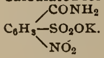
	Calculated for	Found.	
	 $C_6H_3\begin{cases}COOH\\SO_2ONH_4.\\NO_2\end{cases}$	I.	II.
NH_3	6.43	6.39	6.38

Action of Hydrochloric Acid.—On boiling with dilute hydrochloric acid the ammonium salt was hydrolyzed to the acid ammonium salt of paranitroorthosulphobenzoic acid. It was identical with the salt obtained by the action of fuming nitric acid.

	Calculated for	Found.	
	 $C_6H_3\begin{cases}COOH\\SO_2ONH_4.\\NO_2\end{cases}$	I.	II.
NH_3	6.43	6.51	6.41

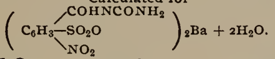
Action of Potassium Hydroxide.—The ammonium salt was boiled with an excess of a dilute solution of potassium hydroxide for six hours. Ammonia was given off during the entire time, showing a slow hydrolysis. On concentrating the solution, the potassium salt of paranitroorthobenzaminesulphonic acid separated. This salt is very soluble in water, and separates in thin yellowish plates. It contains no water of crystallization.

0.1983 gram substance gave 0.0604 gram K_2SO_4.
0.2174 gram substance gave 0.0660 gram K_2SO_4.

	Calculated for	Found.	
	 $C_6H_3\begin{cases}CONH_2\\SO_2OK.\\NO_2\end{cases}$	I.	II.
K	13.73	13.66	13.61

Action of Barium Hydroxide.—A solution of the ammonium salt was treated in the cold with an excess of barium hydroxide. Ammonia was given off and, after the solution had stood for some time, the excess of barium hydroxide was removed by carbon dioxide. From the filtered solution, on evaporation, crystals of the barium salt of paranitrobenzoylureaorthosulphonic acid separated. This salt crystallized in small, yellow prisms and was sparingly soluble in water. It contained two molecules of water of crystallization.

0.3815 gram substance gave 0.0178 gram H_2O.
0.3864 gram substance gave 0.0182 gram H_2O.
0.2778 gram substance gave 0.0906 gram $BaSO_4$.
0.1678 gram substance gave 0.0546 gram $BaSO_4$.



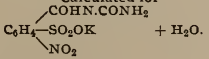
$$\left(C_6H_3\begin{array}{l}\diagup COHNCONH_2\\ -SO_2O\\ \diagdown NO_2\end{array}\right)_2Ba + 2H_2O.$$

	Calculated for	Found.	
		I.	II.
$2H_2O$	4.81	4.66	4.71
Ba	19.20	19.15	19.08

Paranitrobenzoylureaorthosulphonic Acid.—The free acid was made by treating the barium salt with the calculated amount of sulphuric acid. It is a strong acid, very soluble in water, separating out only when the solution is evaporated nearly to dryness. No attempt was made to analyze it.

Potassium Salt.—This salt has a marked crystallizing power, separating out in clusters of long, narrow prisms of a pale-yellow color. It is sparingly soluble in water and crystallizes with 1 molecule of water of crystallization.

0.3573 gram substance gave 0.0181 gram H_2O.
0.5992 gram substance gave 0.0312 gram H_2O.
0.3554 gram substance gave 0.0939 gram K_2SO_4.
0.2289 gram substance gave 0.0612 gram K_2SO_4.

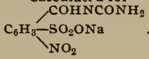


$$C_6H_4\begin{array}{l}\diagup COHN.CONH_2\\ -SO_2OK\\ \diagdown NO_2\end{array} + H_2O.$$

	Calculated for	Found.	
		I.	II.
H_2O	5.22	5.07	5.21
K	11.94	11.85	11.97

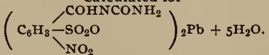
Sodium Salt.—The sodium salt is moderately soluble in water and of a pale-yellow color. It has two habits of crystallization. When a solution of the salt is cooled quickly it separates out in long silky needles, containing 4 molecules of water of crystallization. These give up water very quickly on exposure to the air. When the solution is cooled slowly the salt separates out in orthorhombic prisms containing 1 molecule of water of crystallization. The needles, on standing in the solution, slowly change to the orthorhombic prisms.

0.2893 gram substance gave 0.0158 gram H_2O.
0.2262 gram substance gave 0.0126 gram H_2O.
0.3311 gram substance gave 0.0615 gram H_2O.
0.2637 gram substance gave 0.0484 gram H_2O.
0.2292 gram substance gave 0.0520 gram Na_2SO_4.
0.1878 gram substance gave 0.0432 gram Na_2SO_4.

	Calculated for	Found.	
	 $C_6H_3{<}\begin{matrix}COHNCONH_2\\SO_2ONa\\NO_2\end{matrix}$.	I.	II.
H_2O	5.48	5.46	5.57
$4H_2O$	18.32	18.58	18.36
Na	7.39	7.33	7.40

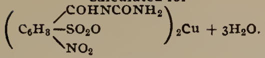
Lead Salt.—This salt is quite soluble in water, separating out in thick, poorly defined prisms of a pale-yellow color. It crystallizes with 5 molecules of water of crystallization, and effloresces on exposure to the air.

0.1043 gram substance gave 0.0106 gram H_2O.
0.2115 gram substance gave 0.0216 gram H_2O.
0.1596 gram substance gave 0.0620 gram $PbSO_4$.
0.2394 gram substance gave 0.0932 gram $PbSO_4$.

	Calculated for	Found.	
	 $\left(C_6H_3{<}\begin{matrix}COHNCONH_2\\SO_2O\\NO_2\end{matrix}\right)_2Pb + 5H_2O.$	I.	II.
$5H_2O$	10.31	10.16	10.21
Pb	26.38	26.50	26.56

Copper Salt.—This salt was made by dissolving freshly prepared copper oxide in a solution of the free acid. It crystallizes in small blue prisms, is quite soluble in water, and contains 3 molecules of water of crystallization.

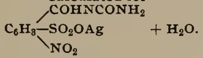
0.1437 gram substance gave 0.0109 gram H_2O.
0.1314 gram substance gave 0.0102 gram H_2O.
0.2969 gram substance gave 0.0374 gram CuO.
0.1691 gram substance gave 0.0170 gram CuO.



	Calculated for	Found. I.	II.
$3H_2O$	7.78	7.59	7.76
Cu	9.91	10.03	10.06

Silver Salt.—The silver salt was prepared by dissolving silver oxide in a solution of the free acid. It crystallizes in long, irregular prisms, is moderately soluble in water, and contains 1 molecule of water of crystallization. It darkens on exposure to light.

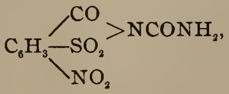
0.1531 gram substance gave 0.0064 gram H_2O.
0.1732 gram substance gave 0.0072 gram H_2O.
0.1622 gram substance gave 0.0444 gram Ag.
0.1438 gram substance gave 0.0392 gram Ag.



	Calculated for	Found. I.	II.
H_2O	4.34	4.18	4.16
Ag	27.27	27.37	27.25

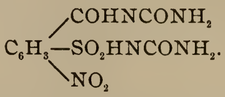
The ammonium salt of paranitrobenzoylureaorthosulphonic acid is a secondary product formed after the heated mass had been dissolved in water. The hydrochloric acid in the aqueous solution probably decomposed the original compound with the formation of ammonium chloride. All attempts to isolate the original compound failed. The mass of chloride and urea, after heating, was extracted with ether and chloroform, but nothing was obtained. It completely dissolved in alcohol, showing that the ammonium salt was not the original compound. It was deliquescent and very soluble in alcohol or water. No intermediate products of the reactions could be isolated.

There are two possible theories to account for the formation of the ammonium salt, as in the case of the ammonium salt of benzoylureaorthosulphonic acid. One molecule of urea may have reacted with 1 molecule of the chloride to form a ureid,



which, on hydrolysis, would take up a molecule of water and give the free sulphonic acid. This, with the ammonium chloride formed from the decomposition of the urea hydrochloride, would give the ammonium salt.

The other explanation is that 2 molecules of urea may have reacted with 1 molecule of the chloride to form a diureid,



$$C_6H_3\left\langle\begin{matrix}COHNCONH_2\\SO_2HNCONH_2.\\NO_2\end{matrix}\right.$$

The urea residue in the sulphonyl group is then hydrolyzed to the ammonium salt. This view seems the more probable.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXX.—ON THE NATURE OF LEAD AMALGAMS.

By Henry Fay and Edward North, 2nd.

Some time ago Gressman[1] published an article on "The Electrical Resistance of Lead Amalgams at Low Temperatures," in which he came to the conclusion that lead and mercury form a series of amalgams in which there is a eutectic alloy. He used amalgams containing from 4 to 25 per cent of mercury and determined the following freezing-points :

Pure mercury	—38°.8
4.2 per cent lead	—37°.7
7.1 " "	—37°.0
11.2 " "	—30°.0
Viscid, 25.0 per cent lead	—37°.65
Eutectic	—40°.0

These points were obtained by measuring the electrical resistance, and calculating from this the temperature at the moment of solidification, which was indicated by a sudden and marked increase in the conductivity of the amalgam as it passed from the liquid to the solid state. The points obtained by Gressman, plotted in the form of a curve, are shown in Fig. 1, in which abscissas represent percentage composition, and ordinates temperatures of freezing.

[1] Phys. Rev., 9, 20.

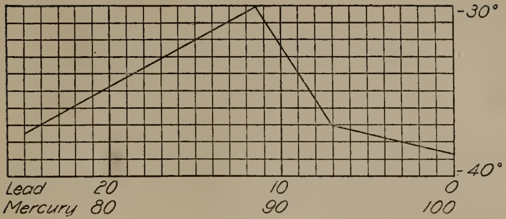


Fig. 1.

It seemed improbable that the mercury-lead amalgams should have such a fusibility curve if the amalgams are in any respect analogous to alloys, which have been shown to be analogous in their behavior to solutions. It is seen that the curve rises to a maximum at 11.2 per cent lead, which would seem to indicate a compound at that point. It then falls rapidly to the 25 per cent amalgam, indicating that it was falling toward a eutectic point. The percentage composition of the eutectic was not given, consequently its point could not be included in the curve. Gressman prepared his eutectic alloy by freezing out part of the amalgam, and then pouring off the portion remaining liquid. It is natural to suppose that in the process of freezing, the lead would separate first, which would, accordingly, concentrate the mercury. If this is actually the case, the percentage of mercury would probably be greater than 75 per cent, and the eutectic point would fall somewhere in the field already plotted. Assuming that the points already plotted are correct, he should have obtained two separate freezing-points for some of his amalgams, one of which would represent the separation of pure lead, pure mercury, or compound, and the other the separation of the eutectic. No such phenomena were observed. With alloys which form eutectic mixtures, and solutions which form cryohydrates, these two points of solidification are very evident. On the other hand, the statement is made that "usually the more lead the amalgam contains, the lower is the melting-point." The direction of the fusibility curve would indicate a minimum point at about 30 per cent lead. This should, then, be about the composition of the eutectic alloy, although the experiments seem to indicate that the eutectic was much richer in mercury. If the eutectic contained as much as 30 per cent of lead, it would be more or less solid at room temperature, which could hardly be expected of a substance melting as low as —40°.

In consideration of the doubt in regard to these points and to the many conflicting statements in the literature in regard to the nature of the amalgams, it was decided to study the subject anew, and to apply those methods which have been of such great value in clearing up the nature of alloys, *viz.*, the establishment of the curve of fusibility, or, what is practically the same thing, the solubility curve, by determining the freezing-points of the amalgams by means of the LeChatelier pyrometer, and the study of the microstructure of the solid amalgams.

The determination of the freezing-point of amalgams by means of the pyrometer is not nearly so satisfactory as it is for alloys on account of their lack of crystalline character. With pure metals, and alloys which are to any extent crystalline, the point of solidification is very clearly marked, but with amalgams the deflection of the galvanometer is not so well marked. When readings of the galvanometer are taken every ten to twenty seconds, the cooling curve shows a retardation at the point of solidification, which cannot be mistaken. The evidence obtained from a study of the microstructure supplements that obtained by an inspection of the fusibility curve.

The fusibility curves of alloys have been found to fall under three general classes:

I. Two metals which form solid solutions give a straight line curve connecting the two melting-points. Examples of this class are the alloys of silver and gold, and bismuth and antimony.

II. Two metals which neither form solid solutions nor compounds, give a two-branch curve meeting in a eutectic point, which is lower than the melting-point of either metal. Typical examples of this class are the alloys of tin with bismuth, lead, and zinc, and the alloys of zinc with aluminium, and cadmium.

III. Two metals which form one or more compounds give a curve, the number of branches of which is $2n + 1$ where n represents the number of compounds. In this class one of the compounds may form a solid solution with one of the pure metals, which would, consequently, modify the character of the curve, and therefore change the number of branches. Examples of this class are the alloys of copper with antimony, tin, and bismuth; those of aluminium and gold, antimony and zinc, and tin and nickel.

The study of the microstructure of these three classes of alloys confirms very decisively the fusibility curves. In the first class it is known that the solvent and dissolved substance separate out together. The microstructure of metals which form solid solutions shows a homogeneous mass in which it is difficult, if not impossible, to distinguish between the two constituents. In the second class, where the freezing-point of the pure metal is considerably lowered by the addition of the other metal, we know that there is first a separation of pure solvent, and as the temperature of the solution is lowered the pure metal continues to separate until the concentration of the resulting solution has reached that of the eutectic alloy when the mass solidifies as a whole. The microscopic constituents, consequently, should be pure metal and the eutectic, the amount of each depending upon the proportion of the two constituents. As the eutectic is the alloy in which the two constituents are each saturated with the other and the two separate simultaneously, we should expect to find a structure made up of alternate layers of the two metals. This is actually found to be the case, and the structure for all eutectics is very characteristic, resembling the fine line markings of the thumb. The eutectic may consist of two metals, a metal and a compound, or two compounds, but in all cases its structure is very characteristic and easily recognized. The presence of compounds in the third class is usually recognized by their crystalline form, the forms of some of them being very characteristic, such as is the case for the compound $SnCu_3$. When, however, a compound forms a solid solution, the detection of the two constituents is much more difficult.

In regard to the existence of compounds in amalgams there is a great variety of statement, and the evidence of their existence is based on a number of methods of investigation, most of which are unsatisfactory. By studies of the specific gravity, specific heat, heat of formation, heat of solution, effect of pressure, and electrical conductivity, the existence of a number of compounds of mercury with the metals is said to have been established, but only in a few cases is the evidence at all conclusive. With more refined methods of investigation, many of the so-called compounds will undoubtedly disappear.

Joule[1] applied a pressure of three tons to the square inch for a day to an amalgam of lead and mercury and obtained a bright crystalline mass, which corresponded closely to the formula Pb_2Hg. Croockewit[2] treated different amalgams with dilute acids and analyzed the portions remaining undissolved. In many cases the results of the analyses agreed closely with the percentages required for certain compounds. For lead amalgams he obtained a residue which corresponds to the composition required by the compound PbHg. Bauer[3] allowed acetic acid and carbon dioxide to act upon an amalgam composed of 2 parts lead and 1 part mercury until neither lead acetate nor lead carbonate were formed. The residue was hard, crystalline, and white. It changed to a bluish-yellow color when exposed to the atmosphere. The composition corresponded to the formula Pb_2Hg_3. Kasantseff[4] studied the action of nitric acid on solid and liquid gold amalgams. He found that the residues which remain do not possess a homogeneous composition, which led him to the supposition that there probably exist hydrargyrates dissolved in mercury, corresponding to the hydrates dissolved in water. The amalgams of gold, lead, and silver were subjected by De Souza[5] to the vapors of boiling mercury, sulphur, and diphenylamine, and they were kept at these temperatures until constant weight was obtained. When heated in boiling sulphur, the residues corresponded to the composition Au_9Hg, $Ag_{13}Hg$; heated in boiling mercury vapor, the residues corresponded to Au_9Hg, $Ag_{11}Hg$, Pb_8Hg; heated in the vapor of diphenylamine the residues were Au_8Hg and Ag_4Hg. Lead, zinc, cadmium, and bismuth amalgams still retained mercury at 360°, but not at 440°. The experiments of De Souza were repeated by Merz and Weith,[1] who modified his methods to some extent, but they were unable to confirm his results. Amalgams were heated for many hours in the vapors of sulphur, mercury, and diphenylamine, carbon dioxide being passed over the amalgams during the heating. The results in nearly all cases gave no evidence of the existence of definite compounds. The gold, silver, copper, bismuth, lead, zinc, and cadmium lost their mercury entirely, or nearly so, at, or in some cases below, the boiling-point of mercury. With those amalgams in which small amounts of mercury were left behind, it was attributed more to mechanical action than to the formation of definite compounds. The most strongly pronounced evidence of chemical compounds was shown by the sodium and potassium amalgams, which lost their mercury only very slowly at the boiling-point of sulphur. On the other hand, as Merz and Weith show, the easy decomposition of the amalgams is not positive proof that compounds do not exist. More positive evidence was obtained in favor of compounds in the amalgams of sodium and potassium by determinations of the melting-points. With sodium they obtained a maximum point with 4.7 per cent of sodium, which melted at 305° to 315°; with potassium, at 9.8 per cent, a maximum was obtained at 240° to 245°. Increase of sodium or potassium lowered the melting-point again.

---

[1] J. Chem. Soc., **16**, 378.

[2] J. prakt. Chem., [1], **45**, 88.

[3] Ber. d. chem. Ges., **4**, 449.

[4] Bull. soc. chim., [2], **30**, 20.

[5] Ber. d. chem. Ges., **8**, 1616; **9**, 1050.

Tammann[2] has pointed out the close relationship between solutions and amalgams, and shows that if on solidification the pure solvent separates, the freezing-point will be lowered, while, on the other hand, if the two constituents separate together, the freezing-point will be higher than that of the solvent. In case of solid solutions the two constituents separate together and the curve of fusibility will connect the two melting-points of the constituents by a straight line. Mazzotto[3] points out the analogy between amalgams and alloys, and shows that while they are similar in most respects their behavior is not identical. They show, on cooling, the various stages, just as alloys do, *viz.*: 1. The mass cools evenly and remains homogeneous and perfectly fluid; 2. The rate of cooling decreases, and at the same time solid particles separate out in the alloy, and increase in number as the temperature falls; 3. The temperature remains constant and the mass solidifies as a whole; 4. The mass again cools evenly. In the second stage Mazzotto finds that pure metals separate from zinc, lead, and bismuth amalgams, while sodium and cadmium deposit solid amalgams of variable composition. As we have not been able to obtain the original paper, it is impossible to state how it was proved that pure metal separates. Mazzotto points out, and it is confirmed by our experiments, that the stop in the third stage of cooling does not take place at a temperature below the freezing-point of the pure metals, as in the alloys, but at the freezing-point of mercury, from which it may be concluded that at this temperature practically no metal remains in solution in the mercury. An exception was found in sodium amalgam which seems to have a eutectic, composed of 5 parts of sodium and 20 parts of mercury by volume, which freezes at —46°. The third stage may be entirely absent in the case of those amalgams which form compounds.

---

[1] Ber. d. chem. Ges., 14, 1438.

[2] Ztschr. phys. Chem., 3, 440.

[3] *Ibid.*, 13, 571, 572.

Recently Puschin[1] has constructed some fusibility curves founded on empirically obtained data, and has come to the conclusion that the amalgams of lead, tin, bismuth, cadmium, and zinc, are all very similar in their nature. He says that none of them seem to show a well-established eutectic point, nor a maximum point indicating a compound. The lowering of the temperature of solidification was found to take place uniformly and uninterruptedly, passing from the heavy metal to mercury. According to Puschin the character of the curve shows that the amalgams of lead, tin, bismuth, zinc, and cadmium form isomorphous mixtures (solid solutions), the varying composition of which is dependent upon the temperature of the separation of the solid phase, and that the formation of such compounds as $HgPb_2$, $HgBi_2$, Hg_2Zn_3, and Hg_2Cd, as described in the literature, is doubtful. Puschin promises to publish later the experimental data of his work, and until then we cannot speak critically of his conclusions, but as the present work has been completed for some time, and has been held back, awaiting the results of some experiments on gold amalgams, we have decided to publish this preliminary paper principally because we have reached different conclusions, having used the same method of experimentation.

---

[1] Russ. Phys. Chem. Soc., **32**, 635; Chem. Ztg., **24**, 950.

The results of our experiments seem to show that in the amalgams of lead and mercury there exists the compound Pb_2Hg, which is soluble in and isomorphous with lead, and it consequently lowers the freezing temperature of lead, as it is successively added to it. This compound is insoluble in mercury and hence does not lower the freezing-point of mercury. The results of the experiments seem to disprove conclusively the statement of Gressman that lead and mercury form a eutectic mixture. This is shown by the absence of any eutectic point in the fusibility curve, and also by the microscopic examination. Reference to Fig. 2, in which the freezing-points have been plotted, the abscissas representing composition and the ordinates temperatures, will show that the lower freezing-points all fall along a straight line drawn slightly above the melting-point of pure mercury.

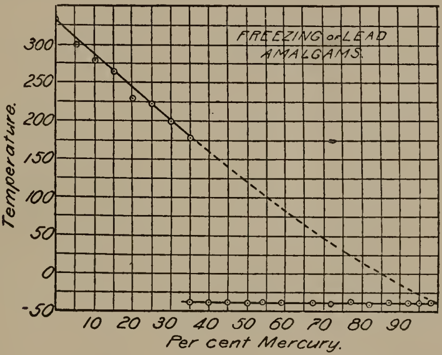


Fig. 2.

The four exceptions which lie below this line occur at wide intervals from each other, and their discrepancy is probably due to slight experimental errors, caused in the variations of the galvanometer from day to day. The existence of a eutectic alloy would have been indicated by a downward slant of the lower branch of the curve, its composition being determined by the point at which the two branches intersected. The lower branch is, however, horizontal.

Another argument against the non-existence of a eutectic alloy is the great similarity in appearance of the microstructure of all the solid amalgams. This includes examination only of those amalgams under 30 per cent of mercury, and on this account the evidence is not entirely satisfactory. The presence of a eutectic, even in small quantities, could hardly fail to make considerable change in the appearance of the structure, especially so if Gressman's statement is true that with increase of lead the freezing-point is lowered. Again, no alloy thus far examined possesses a eutectic freezing at a temperature less than 5° below the freezing-point of its most fusible constituent. Gautier[1] reports several alloys, such as those of lead and copper, nickel and tin, lead and aluminium, and antimony aluminium, in which the melting-point of the eutectic is within a few degrees of the more fusible metal. In the case of lead copper alloys with 0.14 per cent of copper, the melting-point of lead is lowered 2°, while with 0.31 per cent it is raised 4° above the melting-point of lead. This lowering of the melting-point can easily be accounted for by the presence of a small amount of impurity in the lead, and further and more careful study of pure metals will probably show these results to be inaccurate, and the eutectics with melting-points so close to that of the pure metal, which now appear in the alloys named, will disappear. This, of course, does not preclude the possibility that lead and mercury may form a eutectic freezing at 2° below the freezing-point of mercury, but there is little evidence to show that such is the case, while the evidence to the contrary is strong.

It will be seen from Fig. 2 that the higher freezing-points, so far as determined, lie along a straight line, which, if continued as indicated by the dotted portion, would meet the lower horizontal branch at a point corresponding to the freezing of pure mercury. Such a curve, if considered by itself, is that of a solid solution, the freezing-points of which lie along a line connecting the freezing-points of the constituent metals. This portion of the curve may equally well represent the solubility of mercury in lead, and it is seen that up to about 35 per cent of mercury, the freezing-point of lead is successively lowered by the addition of mercury. From the nature of the lower branch it would appear that lead, on the contrary, is not soluble in mercury, and consequently has no effect on the freezing-point of mercury. The solubility of lead in mercury has been determined by Gouy,[1] who found it to be 0.013, which is very small. As will be shown later, this value probably also represents the solubility of the compound Pb_2Hg, the value for which would be 0.018.

---

[1] Bull. de la Société d'Encouragement, [5], 1, 1293.

The nature of the curve is so unusual and so different from any that have heretofore been established, that we have been in some doubt in regard to its explanation, but if we assume the existence of the compound Pb_2Hg and that this compound is only slightly soluble in mercury, the explanation appears to be simple, and, furthermore, is supported by the facts and the general behavior of the amalgams. According to this assumption, the upper branch of the curve shows that the compound is soluble in lead, and lowers its freezing-point as it is formed in larger and larger quantities, with the increase in the amount of mercury.

The microstructure seems to indicate that the two substances are isomorphous, for there is no separation into constituents visible on etching the solid amalgam.

When the percentage of mercury has reached 32.58 per cent there is nothing present but pure compound. If the percentage of mercury is now increased, there is more than enough present to form the compound Pb_2Hg, and mercury becomes the solvent. As the compound is only slightly soluble in mercury, it can have little or no effect upon the freezing-point, and consequently the freezing-points obtained are practically those of pure mercury. They are all slightly above the freezing-point of mercury, with the exception of a few previously mentioned, which would be expected, as the mercury is probably supersaturated with the compound.

---

[1] J. de Physique, 4, 320.

That the compound is insoluble in mercury receives further confirmation from the fact that by pressure Joule obtained a residue which corresponded to the compound Pb_2Hg. All lead amalgams, which are more or less liquid at room temperatures, contain solid particles which may readily be seen. By pressure always the same amalgam is obtained, which, after melting, consists of a crystalline mass in which the edges of the small crystals are rounded off on account of being wetted by the slight excess of mercury. The removal of the mercury which is in excess of that to form the compound Pb_2Hg, may be nicely accomplished by rotating in a centrifugal machine small chamois bags containing liquid amalgam. Under these conditions the excess of mercury is easily removed and the nearly pure compound is left in the bag. An examination of the mercury thus removed shows only traces of lead dissolved in it.

It was not possible to obtain this compound absolutely pure, but the results of a number of analyses show percentages of lead, varying from 66 to 68 per cent. The theoretical percentage is 67.42 per cent lead. Some of the mercury is mechanically held, which make the determinations of lead slightly low.

It will be seen that these phenomena are very similar to those observed in ordinary solutions containing a slightly soluble substance. The solvent, in this case mercury, on account of its great viscosity, is much more difficult to remove completely. Ordinary solvents, however, on account of their extreme limpidity may be easily removed by filtration. Mercury can be separated if sufficient pressure is used. The process of filtering mercury is carried on to a large extent in the gold amalgamation process where the mercury is pressed through buckskin bags, leaving behind a compound of mercury and gold. We have very good evidence that a compound of the formula $AuHg_4$ exists, and perhaps another, the composition of which has not yet been established.

The separation of a compound isomorphous with one of the constituents has a parallel in the field of solutions. Roozeboom has found that the double chloride of ammonia and ferric iron is isomorphous with ammonium chloride, and Le Chatelier has obtained the compound AgCl.NaCl isomorphous with sodium chloride, and the compound $2Na_2SO_4.CaSO_4$ isomorphous with sulphate of sodium. The isomorphism of Pb_2Hg with lead is entirely analogous.

Experimental.

Twenty-one lead amalgams were prepared in which the per cent of lead varied from 2 to 95 per cent. Pure sheet lead, prepared for use in assaying, and chemically pure mercury were used. In making an amalgam, the lead and mercury were weighed to the nearest 0.1 gram, the lead was melted in an annealing cup, the small amount of oxide skimmed off, and the mercury poured in just as the lead began to harden. The amalgam was then thoroughly stirred with a glass rod.

None of the amalgams which contain more than 35 per cent of mercury are entirely liquid. They consist of a liquid and of a pasty, granular, or semisolid portion, which can be easily separated from the liquid part by filtering the amalgam through chamois skin. If considerable pressure is applied, so as to remove all the liquid, or if the liquid is removed by means of a centrifugal machine, there remains a hard, silvery-white amalgam, which is brittle, has a bright granular fracture, and is easily oxidized to a bluish-yellow on exposure to the air. The solid constituent of the amalgams increases in quantity as the percentage of lead increases, and if it does not form too large a proportion of the amalgam, it can apparently be dissolved in the liquid portion by shaking. This, however, is only apparent, as the excess of mercury can readily be removed. On heating, the solid constituent goes into solution, and the temperature at which this takes place is higher as the percentage of the solid increases. These semisolid amalgams are very similar in their behavior to a slush composed of snow and water, from which the liquid portion, water, can be removed by pressure, leaving the more solid ice behind. An amalgam containing about 65 per cent lead is entirely solid. Further addition of lead causes a gradual change from the silvery-white amalgam to the bluish-gray color of pure lead, accompanied by a corresponding increase in the malleability, and a disappearance of the granular fracture.

Cooling and warming curves were run for nearly all of the amalgams. The cooling curves cover the range from the temperatures at which the amalgams are entirely liquid down to room temperature. The warming curves start below the melting-point of mercury and extend to room temperature. The temperatures were measured by means of a thermoelectric couple in connection with a galvanometer of the suspended coil or d'Arsonval type. The junction, composed of a platinum and a platinum-rhodium wire, was protected by a thin piece of hard glass tubing, about 2 mm. in diameter. Inside this tube the wires were insulated by passing over one a fine piece of tubing drawn down from a larger size. The cold junction was enclosed in a bottle surrounded by hair-felt. A thermometer with its bulb in the bottle gave the temperature of the cold junction to 0.1°. The suspended coil of the galvanometer carried a mirror throwing a beam of light on a millimeter scale. The shadow of a vertical wire was read to the nearest 0.1 mm. A scale deflection of 1 mm. was equivalent to a rise or fall in temperature of about 3°. Theoretically, it should have been possible to determine temperatures within 0.3°, but such a degree of accuracy was not practically obtainable. More than half of the freezing-point determinations were made at or near the freezing-point of mercury, and it was highly essential that the results should be reliable, as a variation of a few degrees above or below this temperature, in the freezing of any of the amalgams, might lead to entirely different conclusions. What appeared to be discrepancies, often amounting to 3° or 4°, were noticed in the first series of determinations. Investigation showed that the galvanometer was apt to vary from day to day, the deflection at the temperature of melting mercury often changing by several degrees from one day to the next. It was, therefore, found necessary, in order to obtain satisfactory results, to redetermine the melting-point of mercury three or four times each day, and calculate the freezing-point of each amalgam from the calibration last made. Before and after each experiment the temperature of the cold junction was noted, and the zero reading of the galvanometer, after breaking the circuit.

The galvanometer was calibrated by exposing the couple to the vapors of boiling water (100°), boiling naphthalene (218°.7), and boiling aniline (182°.6) and by placing it in melting mercury (—39°.4). In measuring temperatures below the room temperature the galvanometer connections were reversed in order to give a positive deflection instead of a negative deflection, as would otherwise have been the case.

In order to freeze the amalgams a mixture of ether and solid carbon dioxide was used. The carbon dioxide was obtained in the form of snow by winding a heavy Canton flannel cloth around the orifice and top of a cylinder of the liquefied gas. The tank was laid on its side and the valve opened wide. A few moments sufficed to collect a large amount of snow. This was placed in a beaker surrounded by hair-felt, the whole enclosed in a thick cylinder of cork. Ether was slowly added till the mixture had the consistency of slush. The amalgam, contained in a test-tube, with the thermoelectric couple in its center, was placed in the mixture till frozen solid. When the amalgam was cooled to —75°, the temperature of the freezing mixture, it was quickly removed and placed in a second larger test-tube, so that it was surrounded by an air jacket, and warmed slowly and evenly until room temperature was reached. The warming of the amalgam occupied about twenty minutes, and during this time galvanometer readings were taken every ten seconds.

The solid amalgams, which have a second or higher melting-point, were melted in a small electric furnace made of a porous cup wound with iron wire, the whole surrounded with asbestos and sheathed with wood. When the amalgam was melted the current was shut off and the amalgam allowed to cool slowly in the furnace. Galvanometer readings were taken at intervals of twenty seconds.

The semiliquid amalgams became entirely fluid at comparatively low temperatures (under 150°), and the electric furnace, owing to its size, cooled very slowly at these low temperatures. Therefore, such amalgams were transferred from the freezing mixture to a bath of sulphuric acid, and heated until entirely liquid. For such amalgams only one curve, a warming curve, was plotted, which covers the entire range from a temperature beyond the lowest freezing-point up to one at which the amalgam is entirely liquid. Two amalgams, numbers 9 and 10, were, in addition, melted and cooled in the electric furnace.

The freezing-points of the lead amalgams are given in the following table and are represented graphically in Fig. 2 (p. 223).

Freezing-points of Lead Amalgams Shown Graphically in Fig. 2.

No.	Per cent lead.	Lower freezing-point.	Upper freezing-point.
1	2	—39°.0	
2	5	—39°.0	
3	7	—40°.6	
4	13	—38°.9	
5	18	—42°.0	
6	23	—37°.6	
7	28	—40°.9	
8	33	—39°.0	
9	65.3	—37°.4	185°.2
10	40.8	—39°.1	
11	46	—37°.8	
12	50	—39°.0	
13	55	—39°.6	
14	60	—40°.2	
15	65	—37°.8	177°.3
16	70		199°.4
17	75		221°.0
18	80		229°.0
19	85		263°.7
20	90		278°.5
21	95		299°.3

The results show that the lead amalgams freeze at about the same temperature as pure mercury until the amount of lead reaches 65 per cent. Beyond this point the lower freezing-point disappears, or becomes so indefinite that it does not show, and the amalgams solidify at a temperature which is higher in proportion to the increase in the percentage of lead. Amalgams 9 and 15 possess the upper and lower freezing-points, which may be accounted for by the fact that they are not entirely homogeneous, which is more or less true of all of the amalgams. It will be seen that, with four exceptions, the amalgams having the lower freezing-point all melted at a temperature slightly above the melting-point of pure mercury. These exceptions are widely separated, and are probably due to unavoidable inaccuracies in the temperature measurements caused by the variations of the galvanometer.

In order to examine the solid amalgams under the microscope it was necessary to polish them to a mirror surface. There was considerable difficulty in polishing the amalgams on account of the strong tendency of the mercury to smear the surface when the least pressure was exerted. A mirror surface could, however, be obtained when the surface was first made roughly plane by filing, and then rubbed lightly on a whetstone under water until the file marks disappeared, the final polish being done on wet chamois covered with jeweler's rouge. The most convenient method of obtaining a mirror surface was obtained by casting the melted amalgam on plate glass. This gave a surface which was entirely free from marks and gave a beautiful mirror ready for examination. Numerous etching agents were tried in the endeavor to make a sharp distinction under the microscope between the lead and the mercury. The appearance varied considerably with the different etching agents, but in no case was there a separation into two constituents, as would be expected if lead had separated as pure solvent or if there had been a eutectic mixture. The structure in all cases showed the same general characteristics, becoming coarser as the percentage of mercury increased. The 65 per cent amalgam showed very well developed grains, showing the crystalline nature of the amalgam. The outlines of the grains, however, gave no clue to the crystal system. The different amalgams were compared with some alloys which were known to give isomorphous mixtures, and in general appearance it was difficult to distinguish between them.

Other amalgams are now being studied in this laboratory, and it is hoped that work along similar lines will throw some light on the nature of the amalgams of gold, silver, tin, zinc, and bismuth, concerning which our present knowledge is unsatisfactory.

BOSTON, January 12, 1901.

REPORT.

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS. A SUMMARY.

The question of the dissociating power of different solvents is one of the most important in physical chemistry today. The first step in the study of the physical chemistry of any solvent is to determine accurately its dissociating power, in order that the knowledge obtained may not be simply qualitative but quantitative.

It has often been pointed out that physical chemistry, until quite recently, was almost exclusively the physical chemistry of aqueous solutions. This is due to the fact that water is a good solvent for many substances, that it can be easily obtained in a high degree of purity and kept free from other solvents, and further, that the dissociating power of water can be easily measured. In the last few years, however, a beginning has been made with other solvents, and the first step—the measurement of their dissociating power—taken, at least approximately in a number of cases.

The question of the dissociating power of solvents has acquired additional interest because of certain theories which have been proposed, connecting this property of solvents with other properties, chemical and physical. Thus, J. J. Thomson,[1] and also Nernst,[2] have proposed the theory that the dissociating power of solvents should be very closely connected with their dielectric constants. Brühl[3] thinks that water and similar substances are non-saturated compounds, and refers the large association of their molecules (shown by the surface-tension method of Ramsay and Shields), as well as their large dielectric constant and high dissociating power, to this cause. Ciamician[4] thinks that dissociation is a chemical function of the substance, and those compounds which resemble one another chemically, as water, methyl alcohol, etc., should have the greatest dissociating power. While Konowalow[5] holds the opinion that only those solutions conduct where there is a chemical action between the solvent and the dissolved substance.

The work which has been done will be considered under the following heads: Inorganic solvents, organic solvents, and mixed solvents.

---

[1] Phil. Mag., **36**, 320.

[2] Ztschr. phys. Chem., **13**, 531.

[3] *Ibid.*, **18**, 514: **27**, 319; **30**, 1; Ber. d. chem. Ges., **30**, 163; **28**, 2847; and **28**, 2866.

[4] *Ibid.*, **6**, 403.

[5] Wied. Ann., **49**, 733.

Inorganic Solvents.

Water.—The dissociating power of water has been determined for a large number of substances, by several different methods. The more general methods are: The conductivity method of Kohlrausch,[1] the solubility method of Nernst[2] and Noyes,[3] and the freezing-point methods of Jones,[4] Loomis,[5] and others.

The results obtained by all of these methods agree to within the limit of experimental error. Water, as we shall see, has the highest dissociating power of any solvent thus far obtained in the pure state, and it is probable that there is only one other substance known which, under similar conditions, can ionize substances to the same extent as water.

To determine the dissociating power of solvents other than water, the conductivity method has thus far been chiefly used. In order that the conductivities in other solvents may be compared with those in water, the results for a typical acid, base and salt in aqueous solution are given. The following measurements were made at 18°. The volume v is the number of liters which contains a gram-molecular weight of the electrolyte. μ_v is the molecular conductivity at the volume v.

Hydrochloric acid.		Potassium hydroxide.		Potassium chloride.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
0.1	60.0	0.1	42.3		
0.2	142.0	0.2	99.0		
0.333	201.0	0.333	131.4	0.333	82.7
1.0	278.0	1.0	171.8	1.0	91.9
10.0	324.4	10.0	198.6	10.0	104.7
100.0	341.6	100.0	212.4	100.0	114.7
500.0	345.5	500.0	214.0	500.0	118.5
1000.0	345.5	1000.0	213.0	1000.0	119.3
				5000.0	120.9
				10000.0	120.9

The percentage of dissociation, α, at any dilution is obtained by dividing the value of μ_v at that dilution by the maximum value of μ_v for the substance, which is called μ_∞.

In most solvents it is impossible to determine the value of

---

[1] Wied. Ann., **26**, 160.

[2] Ztschr. phys. Chem., **4**, 372.

[3] *Ibid.*, **6**, 241; **9**, 603; **12**, 162; **16**, 125.

[4] *Ibid.*, **11**, 110, 529; **12**, 623.

[5] Wied. Ann., **51**, 500; **57**, 495, 591; **60**, 523.

μ_∞ directly by the conductivity method, since the dilution at which μ_∞ is reached would be so great that it would not be practicable to apply the conductivity method to it. The best that can be done in such cases is to determine the values of μ_v for varying dilutions and then compare these with the corresponding values in water. In this way an approximate idea of the dissociating power of different solvents can be obtained.

Ammonia.—That solutions of salts in liquid ammonia conduct the current was shown several years ago by Cady.[1] Goodwin and Thompson[2] also made some measurements of the conductivity of such solutions, in connection with their work on the dielectric constant of liquid ammonia, but the most elaborate investigation in this field is that of Franklin and Kraus.[3] They measured the conductivity of potassium bromide and nitrate, sodium bromide and bromate, ammonium chloride and nitrate, silver iodide and cyanide, mercuric cyanide, and a number of organic compounds in liquid ammonia, at dilutions ranging from a few hundred to many thousand liters. A few of their results for three salts are given :

Potassium bromide.		Ammonium chloride.		Silver iodide.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
301.9	210.6	298.9	159.0	314.1	83.5
932.6	259.5	923.4	208.7	951.3	122.7
4099.0	308.5	4059.0	264.7	4034.0	188.2
21480.0	336.1	21270.0	298.8	18200.0	247.5
65040.0	340.2	64400.0	301.4	55120.0	274.0
78430.0	340.4	77660.0	304.4	80000.0	276.0

A direct comparison of the molecular conductivities of salts in liquid ammonia with the molecular conductivities in water at the same dilutions, will show that the former values are much larger than the latter. This would seem to indicate, at first sight, that ammonia has a greater dissociating power than water, but such is not the case. It will be observed that the conductivities in water are measured at 18°, or 82° below its boiling-point, while the conductivities in liquid ammonia are measured at its boiling-point —38°. The conductivities in liquid ammonia should be compared with the conductivities in water at its boiling-point, and the latter values would be, in many cases, more than double the conductivities in water at 18°.

Further, if the molecular conductivities in liquid ammonia should even be greater than in water under comparable conditions, this alone would not show that the dissociating power of ammonia was greater than that of water. The percentage of dissociation, $\alpha = \frac{\mu_v}{\mu_\infty}$. μ_v might be larger in ammonia than in water, and the difference between the two values of μ_∞ might be even greater, so that μ_∞ would be smaller in ammonia. Such is the fact. The high value of the molecular conductivity in ammonia is due rather to the great velocity with which the ions move through this solvent than to the large number of ions present.

---

[1] J. Phys. Chem., **1**, 707.

[2] Phys. Rev., **8**, 38.

[3] This Journal, **23**, 277; **24**, 83.

Nitric Acid.—Bouty[1] has shown that the conductivity of certain alkaline nitrates dissolved in nitric acid is very large, being of nearly the same magnitude as in water. The work is far too incomplete to enable us to draw any conclusion as to the relation between the dissociating power of nitric acid and of water. The dissociating power of the acid is, probably, very great.

Sulphur Dioxide.—That liquid sulphur dioxide has the power to dissociate salts into their ions is shown by the work of Walden,[2] on the conductivity of solutions in this solvent. He worked with seven iodides, one bromide, and two sulphocyanates, and measured their conductivities at 0°, in dilutions ranging from a few liters to 100 or 200 liters. A few of his results are given :

Potassium bromide.		Ammonium iodide.		Potassium sulphocyanate.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
14.6	30.9	20.3	36.3	10.4	17.4
29.4	30.5	30.2	37.6	22.2	17.8
38.6	31.7	54.8	43.5	36.3	19.2
50.2	33.2	91.5	49.2	53.9	20.9
71.5	35.4			73.0	22.9

Walden compared these values with those of the corresponding salts in water at 0°, and found that the conductivities in liquid sulphur dioxide are from one-fourth to one-half the conductivities in water, under the same conditions.

He determined also the molecular weights of a number of salts in liquid sulphur dioxide, by the boiling-point method, and obtained the surprising result that many of the substances which conducted, gave abnormally large molecular weights. Some results which are analogous to these were obtained by

---

[1] Compt. rend., **106**, 595.

[2] Ber. d. chem. Ges., **32**, 2862.

Franklin and Kraus[1] in liquid ammonia as the solvent. The probable explanation is that while there is some dissociation into ions, there are also molecular aggregates present of a high degree of complexity. This would account for the facts observed.

Sulphur Dichloride, *Sulphuryl Chloride*, *Thionyl Chloride*, *Phosphorus Oxychloride*, *Arsenic Trichloride*, *Antimony Trichloride.*—Walden[2] has quite recently studied the dissociating power of the above-named solvents, and finds that all of them break down electrolytes into their ions to a marked extent. An example or two will suffice:

Tetraethylammonium iodide in phosphorus oxychloride.

v.	μ_v.
250	28.91
500	33·45
750	26.11
1500	41.60

Trimethylsulphine iodide in arsenic trichloride.

v.	μ_v.
250	51·44
500	57·90
750	60.75
1500	66.60

Walden also studied solutions of salts in boron trichloride, phosphorus trichloride, phosphorus tribromide, antimony pentachloride, silicon tetrachloride, stannic chloride, sulphur trioxide, and bromine, and found that these substances have little or no ionizing power. Phosphorus trichloride cannot dissociate electrolytes, while phosphorus oxychloride has a strong ionizing power; similarly, antimony pentachloride cannot dissociate electrolytes, while the trichloride dissociates to a very considerable extent. We, therefore, cannot draw any conclusion in reference to the dissociating action of a solvent, knowing the dissociation in solvents which are closely allied to it chemically.

Organic Solvents..

Methyl Alcohol.—When we turn to the organic solvents, we find that considerable work has already been done on the conductivity of electrolytes dissolved in some of them. This is especially true of methyl and ethyl alcohols. Fitzpatrick[3] studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride, and calcium chloride in methyl alcohol, and found values which, though less than in water, were very considerable. Hartwig[1] measured the conductivity of formic, acetic, and butyric acids in methyl alcohol. Paschkow[2] studied the conductivities in methyl alcohol of potassium iodide, cadmium iodide, calcium nitrate, and potassium and sodium acetates. Völlmer[3] worked out the conductivities of potassium and sodium iodides, potassium and sodium acetates, and lithium chloride in methyl alcohol, for a considerable range of dilution. Holland[4] studied the effect of non-electrolytes on the conductivity in methyl alcohol of potassium, sodium, calcium, lithium, and ammonium nitrates, and sodium chloride. Carrare[5] carried out, by far, the most extensive investigation of salts in methyl alcohol which has yet been made. He measured the conductivities of the following substances at various dilutions: sodium chloride, iodide, methylate, acetate; lithium chloride, potassium chloride, bromide, iodide, methylate; ammonium chloride, bromide, iodide, and fluoride; tetraethylammonium chloride, bromide and iodide, tetramethylammonium iodide, triethylamine, diisopropylamine, and a number of sulphur derivatives. The conductivities in methyl alcohol of lithium and calcium chlorides, lithium, sodium, and barium bromides, potassium iodide, ammonium nitrate, and potassium acetate were determined by Kerler[6] in Beckmann's laboratory. The conductivity of mercuric iodide in methyl alcohol was measured by Cattaneo;[7] Schall[8] determined the conductivity of hydrochloric, picric, oxalic, and dichloracetic acids in methyl alcohol; Kablukoff[9] also studied the conductivity of hydrochloric acid in methyl alcohol; and Kahlenberg and Lincoln[10] measured the conductivities of ferric chloride and antimony trichloride in this solvent.

---

[1] This Journal, **20**, 848.

[2] Ztschr. phys. Chem., **25**, 209.

[3] Phil. Mag., **24**, 378.

The most satisfactory work, on the whole, which has ever been done on the conductivity of solutions in methyl alcohol, is that of Zelinsky and Krapiwin.[11] Their work included a number of salts in pure methyl alcohol, as well as in a mixture of methyl alcohol and water, as we shall see later. They used in their work potassium bromide and iodide, ammonium bromide and iodide, cadmium iodide, tetramethylammonium bromide and iodide, tetraethylammonium iodide, a number of the substituted amines and sulphines, diethyl- and triethylstannic iodides, "fumaroid" dimethylsuccinic acid, oxalic acid, iodic acid, and trichloracetic acid.

---

[1] Wied. Ann., **33**, 58; **43**, 838.

[2] Charkow, 1892.

[3] Wied. Ann., **52**, 328.

[4] *Ibid.*, **50**, 263.

[5] Gazz. chim. ital., **26** (1), 119.

[6] Dissertation, Erlangen, 1894.

[7] Rend. R. Acc. Linc. Roma, 1895.

[8] Ztschr. phys. Chem., **14**, 701.

[9] *Ibid.*, **4**, 429.

[10] J. Phys. Chem., **3**, 26.

[11] Ztschr. phys. Chem., **21**, 35.

A few of the results obtained by Zelinsky and Krapiwin are given below. These suffice to show the relation between the conductivities in methyl alcohol and in water (see p. 233).

Potassium bromide.		Ammonium iodide.		Hydroxylamine hydrochloride.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
32	69.02	16	72.24	16	54.39
64	76.70	32	78.74	32	62.18
128	83.60	64	85.0	64	69.52
256	88.96	128	91.14	128	75.98
512	93.26	256	96.20	256	81.21
1024	97.25	512	100.6	512	85.15
2048	100.1	1024	104.7	1024	87.30
4096	101.4			2048	85.70

Comparing these values of the molecular conductivity in methyl alcohol, with those of potassium chloride at the same dilution in water, we see that they are not very different. The conductivity in methyl alcohol is about two-thirds to three-fourths that in water, under the same conditions.

An examination of the above results will show that even in as strong a dissociant as methyl alcohol, it is almost impossible to reach the value of μ_∞ directly by the conductivity method. That dilution at which the salt would be completely dissociated by this solvent is so great that it is impossible to apply the conductivity method to it with any degree of accuracy. It is, therefore, not possible to measure dissociation accurately, even in methyl alcohol, by the conductivity method.

Another method has been used by Jones[1] to measure the dissociation of salts by methyl alcohol. He so improved the boiling-point method that it can be used to measure dissociation in a solvent like methyl alcohol to a fair degree of accuracy. The salts used were potassium, sodium, and ammonium bromides; potassium, sodium, and ammonium iodides; potassium and sodium acetates; and calcium nitrate. The dissociation in methyl alcohol, as found by the boiling-point method, is, in round numbers, about two-thirds of that in water under the same conditions.

Ethyl Alcohol.—The number of those who have worked on solutions in ethyl alcohol is quite as large as in methyl alcohol. Fitzpatrick[1] measured the conductivities of solutions of calcium chloride, calcium nitrate, lithium chloride, lithium nitrate, mercuric, magnesium, and ferric chlorides. Hartwig[2] determined the conductivity of formic, acetic, and butyric acids in alcohol. Vicentini[3] used the following chlorides: ammonium, lithium, magnesium, calcium, cadmium, zinc, and cupric, while Cattaneo[4] studied mercuric, ferrous, and ferric chlorides, cadmium bromide, and cadmium iodide. Cattaneo found that these substances have a negative temperature coefficient of conductivity. Völlmer[5] used a larger number of salts in ethyl alcohol than in water. These were potassium and sodium iodides, potassium and sodium acetates, sodium, lithium and calcium chlorides, and calcium and silver nitrates. Kawalki[6] compared the diffusion of a series of salts in water and in ethyl alcohol, and found that the rates of diffusion in the two solvents bore the same relation as the maximum molecular conductivities in these solvents. Reference should be made to the work of Paschkow,[7] who measured the conductivities in ethyl alcohol of potassium and cadmium iodides, potassium and sodium acetates, and calcium nitrate; of Schall,[8] who worked with picric, oxalic, and dichloracetic acids; of Wildermann,[9] who studied the conductivities of di- and trichloracetic acids; of Kahlenberg and Lincoln,[10] whose work in ethyl alcohol included ferric chloride and antimony trichloride; and of Kablukoff,[11] who measured the conductivity of hydrochloric acid in ethyl alcohol. The results obtained by Kahlenberg and Lincoln for the two chlorides with which they worked are given below:

---

[1] Ztschr. phys. Chem., 31, 114.

Ferric chloride.		Antimony trichloride.	
v.	μ_v.	v.	μ_v.
2.89	9.91	8.11	4.18
11.57	13.70	32.45	7.94
46.28	15.50	64.91	12.30
195.12	19.33	129.81	18.23
390.24	21.20	259.62	29.43

---

[1] Phil. Mag., **24**, 378.

[2] Wied. Ann., **33**, 58; **43**, 838.

[3] Biebl. Wied. Ann., **9**, 131.

[4] *Ibid.*, **18**, 219, 365.

[5] Wied. Ann., **52**, 328.

[6] *Ibid.*, **52**, 324.

[7] Dissertation, Charkow, 1892.

[8] Ztschr. phys. Chem., **14**, 701.

[9] *Ibid.*, **14**, 267.

[10] J. Phys. Chem., **3**, 26.

[11] Ztschr. phys. Chem., **4**, 429.

The dissociation of a number of salts in ethyl alcohol, as in methyl alcohol, has been measured by Jones,[1] using the boiling-point method. These include potassium and sodium iodides, sodium and ammonium bromides, potassium and sodium acetates, and calcium nitrate. These salts were found to be dissociated by ethyl alcohol to from one-third to one-fourth the extent to which they are dissociated by water, at the same dilution. It should be observed that dissociation as measured by the boiling-point method may not be directly comparable with dissociation as measured by the conductivity method, since the two sets of measurements are made at very different temperatures. It, however, seems very probable, from work which is now in progress in this laboratory, that the temperature coefficient of dissociation is quite small, in which case there should be only a small difference between the results obtained by the two methods.

Propyl and Allyl Alcohols; Isopropyl, Isobutyl, and Isoamyl Alcohols.—The dissociating power of alcohols higher in the series than ethyl alcohol has been determined for only a very few substances. A little work has, however, been done on the conductivity of a few electrolytes in the alcohols mentioned above. Schlamp[2] measured the conductivity in propyl alcohol of solutions of lithium and calcium chloride, sodium iodide, and lithium salicylate, and compared the results with those obtained in ethyl alcohol and in water. The conductivity in propyl alcohol is somewhat less than 0.5 that in ethyl alcohol, under the same conditions of concentration and temperature. Carrara[3] made a few measurements of conductivity in propyl and amyl alcohols, and Hartwig[4] determined the conductivity of formic, acetic, and butyric acids in amyl alcohol. The conductivity of triethylsulphine iodide in isopropyl alcohol was determined by Carrara.[5]

Two substances have been studied in isobutyl alcohol; hydrochloric acid by Kablukoff[6] and picric acid by Schall.[7] Their results are given below:

Hydrochloric acid in isobutyl alcohol.

v.	μ_v.
0.49	2.15
2.56	3.08
50.33	3.84
136.62	3.99

Picric acid in isobutyl alcohol.

v.	μ_v.
101.6	1.48
307.4	1.91
511.0	2.20
638.0	2.30

[1] Ztschr. phys. Chem., **31**, 133.

[2] Ztschr. phys. Chem., **14**, 272.

[3] Gazz. chim. ital., **27**, I, 221.

[4] Wied. Ann., **33**, 48; **43**, 838.

[5] Gazz. chim. ital., **27**, I, 221.

[6] Ztschr. phys. Chem., **4**, 432.

[7] Ztschr. phys. Chem., **14**, 707.

Kablukoff[1] also worked with solutions of hydrochloric acid in isoamyl alcohol, and obtained the following results:

Hydrochloric acid in isoamyl alcohol.

v.	μ_v.
3.42	1.79
5.44	1.66
8.93	1.47
14.29	1.42
25.42	1.25

The above results bring out the remarkable fact that the molecular conductivity of hydrochloric acid in isoamyl alcohol decreases with increase in dilution. This is the first time we have encountered such a relation.

Ether.—Very little has thus far been done on the conductivity of ethereal solutions. Cattaneo[2] has measured the conductivity of ethereal solutions of cadmium iodide, cadmium bromide, ferrous and ferric chlorides, aluminium, mercurous and stannous chlorides, salicylic acid, and hydrochloric acid. The conductivities were determined at temperatures ranging from 10° to 30°, and it was found that the conductivity decreased with rise in temperature—ethereal solutions have a negative temperature coefficient of conductivity. Cattaneo also found that the molecular conductivity of hydrochloric acid in ether decreased with increase in dilution. This is analogous to the results obtained by Kablukoff, who found a similar result for hydrochloric acid in isoamyl alcohol. Indeed, Kablukoff[3] found also that the conductivity of hydrochloric acid in ether decreased with the dilution.

Acetone and Other Ketones.—The conductivities of a number of salts of the alkalies in acetone were published by Cattaneo[4] some five years ago. About the same time a paper appeared by St. v. Laszczynski[5] on the conductivity of solutions of some salts in acetone. A number of salts were included: Lithium and mercuric chlorides, potassium iodide, silver nitrate, and potassium, sodium, and ammonium sulphocyanates. The conductivity of solutions in acetone has also been measured by Carrara;[6] but the following results are taken from the work of von Laszczynski.

---

[1] Ztschr. phys. Chem., **4**, 429.

[2] Atti. R. Acc. delle Scienze, Torino, **28**, 329; Rendic R. Acc. dei Lincei, (5), **2**, 1 sem., 295.

[3] Ztschr. phys. Chem., **4**, 431.

[4] Rend. R. Acc. dei Lincei, (5), 4^{o}, 2^{e} sem., 63–75.

[5] Ztschr. elek. Chem., 1895, 55.

[6] Gazz. chim. ital., **27**, I, 207.

Lithium chloride.		Potassium sulphocyanate.		Silver nitrate.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
12.44	4.58	2.04	24.4	143.9	13.3
24.88	6.61	4.08	34.5	287.8	14.7
49.76	9.40	8.16	44.2	575.6	16.5
99.52	12.9	16.32	55.1		
		32.64	66.6		

Kahlenberg and Lincoln[1] measured the conductivity of solutions of ferric, cupric, and stannous chlorides, and antimony trichloride, in acetone ; and Dutoit and Aston,[2] as well as Dutoit and Friderich,[3] studied a number of solutions in acetone and other ketones. Dutoit and Aston pointed out that those solvents which dissociate to the greatest extent are polymerized, as is shown by the surface-tension method of Ramsay and Shields.[4] They raise the question as to whether there is not a necessary relation between the polymerization of the solvent and its dissociating power. To test this they measured the conductivity of salts in a number of solvents. In acetone they used cadmium iodide and sodium salicylate.

In addition to acetone they worked with methylethylketone and methylpropylketone. In the former solvents they used mercuric chloride, cadmium iodide, ammonium sulphocyanate, and sodium salicylate ; in the latter, cadmium iodide, ammonium sulphocyanate, and sodium salicylate. They found larger conductivity in the methylethyl- than in the methylpropylketone, but the conductivity in acetone was greater than in methylethylketone. The following data will illustrate these statements:

	Acetone.	Methylethyl-ketone.	Methylpropyl-ketone.
	μ_v.	μ_v.	μ_v.
CdI_2 ($v = 64$)	11.6	5.58	2.13
" ($v = 128$)	11.9	5.48	1.55

Dutoit and Aston conclude from their work, together with that of Kablukoff,[5] that there is a general relation between the polymerization of the molecules of a solvent and its dissociating power.

The work of Dutoit and Friderich[6] confirms that of Dutoit and Aston. They find that the values of μ_∞ for any electrolyte in different solvents, is a direct function of the amount of polymerization of the molecules of the solvent, and inversely as the coefficients of viscosity of the solvents.

---

[1] J. Phys. Chem., 3, 27.

[2] Compt. rend., 125, 240.

[3] Bull. soc. chim., [3], 19, 321.

[4] Ztschr. phys. Chem., 12, 433.

[5] *Ibid.*

[6] Bull. soc. chim., [3], 19, 321.

In connection with their work in acetone as the solvent they make this remarkable statement :[1] " We have found by the boiling-point method that the following salts in acetone have normal molecular weights : Cadmium iodide, lithium chloride, sodium iodide, mercuric chloride, and ammonium sulphocyanate." and these substances in acetone conduct the current. Some results already obtained in this laboratory seem to throw light on this apparent discrepancy.

Formic and Acetic Acids.—Quite an elaborate investigation on the dissociating power of formic acid was carried out by Zanninovich-Tessarin.[2] He used chiefly the freezing-point method, but also determined the conductivity of a few salts in this solvent. He measured the freezing-point lowering of formic acid produced by the following substances, at dilutions ranging from 0.34 to 3.4 normal (and in some cases at even greater concentration) : Potassium, sodium, ammonium, and lithium chlorides ; potassium, sodium, and ammonium bromides ; hydrochloric, acetic, and trichloracetic acids. A few of his results are given :

Potassium chloride.		Sodium bromide.		Hydrochloric acid.	
Concent. normal.	Diss. Per cent.	Concent. normal.	Diss. Per cent.	Concent. normal.	Diss. Per cent.
0.341	74	1.522	51	1.82	0
1.055	62	2.509	54	2.20	0
2.263	63	4.995	60		

Formic acid is, thus, one of the strongest dissociating solvents next to water. The behavior of hydrochloric acid in this solvent is very surprising. It not only shows no dissociation in formic acid, but the molecules are actually polymerized. The conductivities of potassium and sodium chlorides in formic acid were found to be very large, and hydrochloric acid showed considerable conductivity in this solvent, although the freezing-point lowering indicated polymerization instead of dissociation. This may be due to the fact that while most of the molecules were polymerized into very large complexes, some few were dissociated into ions which carried the current.

Zanninovich-Tessarin[3] also determined the freezing-point lowering of acetic acid produced by sodium bromide and lithium chloride. The former gave normal values, indicating no dissociation, while the latter showed very marked polymerization.

The conductivity of sulphuric acid in acetic acid has been measured by Jones,[1] who found that the molecular conductivity, which was small at all dilutions, increased with the dilution to a certain point ($v = 3$), and then decreased with further increase in the dilution of the solution. This is somewhat analogous to the result obtained by Kablukoff[2] for hydrochloric acid in ether and in isoamyl alcohol.

---

[1] Bull. soc. chim., 334.

[2] Ztschr. phys. Chem., **19**, 251.

[3] *Ibid.*, **19**, 255.

The Nitriles.—The conductivities of mercuric chloride, sodium bromide, cadmium bromide and iodide, ammonium sulphocyanate and silver nitrate, in propionitrile, were determined by Dutoit and Aston.[3] This investigation was extended by Dutoit and Friderich[4] to solutions in acetonitrile and butyronitrile. The dissociating power of these three related substances can be seen from the following figures :

Silver nitrate.	Acetonitrile.	Propionitrile.	Butyronitrile.
	μ_v.	μ_v.	μ_v.
$v = 8$	54.5	14.21	....
$v = 128$	118.3	34.42	23.8
$v = 256$	131.5	38.86	35.5

The dissociating power is obviously greater in the first members of the series of nitriles, and becomes less as we ascend the series.

Pyridine.—Our knowledge of the dissociating power of pyridine we owe almost entirely to St. v. Laszczynski and St. v. Gorski.[5] They measured the conductivities of lithium chloride, potassium, sodium, and ammonium iodides, and potassium, sodium, and ammonium sulphocyanates in pyridine, over a wide range of dilutions. A few of their results are given :

Potassium iodide.		Sodium sulphocyanate.	
v.	μ_v.	v.	μ_v.
178.49	22.04	32.24	7.98
713.9	30.68	128.96	12.79
2855.6	38.05	515.84	20.56

The conductivities are very considerable in this solvent.

Werner[6] found that certain inorganic salts in pyridine conduct very well, and yet show little or no dissociation by the boiling-point method.

---

[1] This JOURNAL, **16**, 13.

[2] *Loc. cit.*

[3] Compt. rend., **125**, 240.

[4] Bull. soc. chim., (3), **19**, 321.

[5] Ztschr. elek. Chem., **4**, 290.

[6] Ztschr. anorg. Chem., **15**, 1, 39.

Other Organic Solvents.—A few measurements of the conductivity of one or more substances in a number of solvents have been made, but the work with any one of the remaining solvents is so slight that it does not call for special treatment. Thus, Werner[1] found that cuprous chloride in ethyl sulphide conducts very poorly. Cattaneo[2] studied a few solutions in glycerine and found that they had larger conductivity than the corresponding solutions in ether. They also had larger temperature coefficients of conductivity. Kablukoff[3] measured the conductivity of hydrochloric acid in benzene, xylene, and hexane, and showed that solutions in the hydrocarbons conduct very poorly.

Dutoit and Aston[4] measured the conductivity of electrolytes in benzene chloride, ethyl iodide, ethyl bromide, and amyl acetate, and found that solutions in these solvents conducted very poorly. They found, on the other hand, that solutions in nitroethane conduct very well. Dutoit and Friderich[5] worked with acetophenone as solvent, and with cadmium iodide, mercuric chloride, and ammonium sulphocyanate as electrolytes. The conductivity in this solvent was small.

Four other solvents have thus far been studied—ethyl acetate, ethyl acetoacetate, benzaldehyde, and nitrobenzene. This work has been done by Kahlenberg and Lincoln.[6] As electrolytes they used ferric and stannous chlorides, bismuth trichloride, and antimony trichloride. The conductivities in these solvents are, in general, small, but vary considerably with the nature of the electrolytes used.

Mixed Solvents.

Hydrogen Dioxide and Water.—The dissociating power of a mixture of hydrogen dioxide and water has not yet been measured, but Calvert[7] has found that the dielectric constant of such mixtures is greater than that of pure water. He employed the beautiful method of Drude, and from the dielectric constant of the mixture he calculated the dielectric constant of pure hydrogen dioxide to be 92.8 at 18°. The dielectric constant of pure water at this temperature is, according to Drude, 81.

J. J. Thomson[8] pointed out, as has already been mentioned, that there is probably a very close relation between the dielectric constants of solvents and their dissociating power. We shall see that while the two are not proportional, there is undoubtedly a qualitative relation between them. It is, therefore, very probable that the dissociating power of hydrogen dioxide is greater than that of water. This would not be very surprising, since many of the properties of hydrogen dioxide are simply the properties of water intensified. Work on this problem is now in progress in this laboratory.

---

[1] Ztschr. anorg. Chem., **15**, 1, 39.

[2] Beibl. Wied. Ann., **17**, 365.

[3] Ztschr. phys. Chem., **4**, 429.

[4] Compt. rend., **125**, 240.

[5] Bull. soc. chim., [3], **19**, 325.

[6] J. Phys. Chem., **3**, 12.

[7] Ann. der Phys., **1**, 483.

[8] *Loc. cit.*

Mixtures of Water and the Alcohols.—A number of experimenters have worked with mixtures of water and one or another of the alcohols. We should mention the work of Lenz,[1] Stephan,[2] Kerler,[3] Kablukoff,[4] Carrara,[5] Schall,[6] and Arrhenius.[7] Quite an elaborate investigation on the conductivity of electrolytes in mixtures of water and ethyl alcohol, was carried out by Wakeman.[8] His work had to do chiefly with the organic acids in mixtures of these solvents containing varying amounts of alcohol. The results showed that the conductivity became gradually smaller as the amount of alcohol present became larger and larger—just as would be expected from the relative conductivities in these two solvents.

But results of a very different character were obtained by Zelinsky and Krapiwin[9] in mixtures of methyl alcohol and water. It will be remembered that electrolytes in methyl alcohol conduct, in general, to a much smaller degree than in water; yet certain salts were found to have greater conductivity in pure methyl alcohol than in a mixture of 50 per cent methyl alcohol and 50 per cent water. This is shown by the following table, taken from the work[10] of Zelinsky and Krapiwin:

---

[1] Mem. de l'Acad. de St. Petersbourg, (7), **30**, 1881.

[2] Wied. Ann., **17**, 673.

[3] Dissertation (Erlangen), 1884.

[4] Ztschr. phys. Chem., **4**, 432.

[5] Gazz. chim. ital., **16**, 1.

[6] Ztschr. phys. Chem., **14**, 701.

[7] *Ibid.*, **9**, 487.

[8] *Ibid.*, **11**, 49.

[9] *Ibid.*, **21**, 35.

[10] *Ibid.*, **21**, 49.

Potassium Bromide.

	Water.	Methyl alcohol.	Methyl alcohol, one-half; water, one-half.
v.	μ_v.	μ_v.	μ_v.
16	123.1	....	59.82
32	127.5	69.02	62.46
64	130.5	76.70	65.36
128	132.9	83.60	67.11
256	136.4	88.96	69.26
512	140.2	93.26	70.53
1024	143.4	97.25	....

Ammonium Iodide.

16	125.4	72.24	62.63
32	129.6	78.74	65.04
64	133.4	85.0	67.48
128	135.9	91.14	69.28
256	138.7	96.20	70.34
512	141.3	100.6	71.12
1024	143.7	104.7	71.57

It is impossible at present to say what these surprising and very remarkable results mean. They are confirmed by the work of Kerler and of Carrara.

Similar results were obtained by Cohen[1] with ethyl alcohol and water, but only when the mixture contained very little water and at dilutions which were quite large, as is shown by the following table:

Potassium Iodide.

	Pure alcohol.	80 parts alcohol and 20 parts water.
v.	μ_v.	μ_v.
64	26.1	30.9
128	29.2	32.2
256	31.8	33.2
512	34.4	34.1
1024	36.0	34.5
2048	36.3	35.0

The conductivity in the mixture is the greater, until a dilution of 512 liters is reached, when the conductivity in the pure alcohol becomes greater than in the alcohol containing 20 per cent of water.

Cohen found, however, for most substances that the presence of water in the alcohol increased the molecular conductivity, as we would expect.

---

[1] Ztschr. phys. Chem., 25, 31.

Conclusions from the Work thus far Done.

An examination of the work described in this review will show that different solvents have very different ionizing power. With the possible exception of hydrogen dioxide water is the strongest ionizer. Next to this comes formic acid. Of the more common solvents, methyl alcohol dissociates to a much greater degree than ethyl alcohol. Indeed, it is true, in general, that *in an homologous series of solvents the lower members have the greater dissociating power.*

It has already been mentioned that attempts have been made to discover relations between the ionizing power and other properties of a solvent. Thomson's theory that the dissociating power and the dielectric constants of solvents should stand in very close relation to each other, undoubtedly contains a large element of truth. Those solvents which have the largest dissociating power, have, in general, the largest dielectric constants. A number of independent investigations have shown that these two properties are not proportional.

The suggestion of Dutoit and Aston that there is a connection between the amount of association of the molecules of a solvent, and its power to ionize electrolytes, undoubtedly contains much truth. Thus, the molecules of water are associated to a greater extent than those of any other liquid, as Ramsay and Shields have shown. The molecule of liquid water at ordinary temperatures is $(H_2O)_4$. Similarly, the alcohols and other strongly dissociating solvents show considerable association of their molecules.

It will probably be shown that the dissociating power of a solvent is not a function of any one physical or chemical property of the substance, but of them all. Or, perhaps, more accurately expressed, all the properties of a substance are a function of the energy relations which obtain in that substance, and ionizing power is simply one of these properties.

The conclusion from this work which is of chief importance for pure chemistry is that ions are almost always present when chemical reaction takes place. When the number of solvents which can effect ionization to some extent is considered, and the fact that heat and possibly pressure can dissociate molecules, it will be seen that there is scarcely a chemical reaction in which ions, as well as molecules, are not present. The question then arises: Which causes the reaction, the ions or the molecules? This can be answered by excluding ions and then observing whether chemical reaction takes place or not. This has been done with the following results: Hydrochloric acid gas dried and dissolved in dry chloroform does not conduct the current and is, therefore, not dissociated. Under such conditions it will not decompose carbonates. Liquid hydrochloric and sulphuric acids when free from water will not turn litmus red. Dry hydrochloric acid gas and dry ammonia gas do not react to the slightest extent. Still more surprising, perhaps, is the fact that sulphuric acid free from water will not react upon dry metallic sodium. Special precautions must be taken, of course, in all such cases to remove every trace of moisture.

The above examples might be largely increased, but these suffice to show the chemical inertness of molecules. We are now in a position to say that most chemical reactions, if not all, are reactions between ions, and molecules as such do not enter into the reactions at all. As the reactions proceed and the ions already present are used up, the molecules are gradually dissociated and furnish new ions which then enter into the reaction. The chemistry of atoms and molecules has thus given place to the chemistry of ions. HARRY C. JONES.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January 1, 1901.

REVIEWS.

A MANUAL OF ASSAYING: The Fire Assay of Gold, Silver and Lead, Including Amalgamation and Chlorination Tests. BY ALFRED STANLEY MILLER, Professor of Mining and Metallurgy, University of Idaho. First Edition. New York: John Wiley and Sons. 91 pp. $1.00.

The author's preface says "The plan of this book is a departure from the books on this subject with which the writer is familiar. The apparatus is brought in where its use is easily understood. The student is taught the operations of the fire assay by practising with an ore easy to assay. He is then better prepared to understand the directions for assaying more complex ores."

The author has succeeded admirably; he notes and explains all the details which confuse a beginner, and the student is led onward step by step.

This little work may be recommended as a college manual; it contains enough for the college student, and covers its limited subject fully. E. R.

A TEXT-BOOK OF IMPORTANT MINERALS AND ROCKS, with Tables for the Determination of Minerals. BY S. E. TILLMAN, Professor of Chemistry, Mineralogy, and Geology, U. S. Military Academy, West Point, N. Y. First Edition. New York: John Wiley and Sons. 186 pp. $2.00.

This book comprises a brief descriptive chapter on the elements of crystallography, another on the physical and chemical properties of minerals, another devoted to descriptive mineralogy, a set of tables for the determination of minerals, and a brief chapter on common rocks. It is, in short, a condensed manual of determinative mineralogy adapted to the needs of an institution where a book like that of Brush and Penfield would be too large. E. R.

ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY, AND BLOWPIPE ANALYSIS FROM A PRACTICAL STANDPOINT. By ALFRED T. MOSES AND CHARLES LATHROP PARSONS. Enlarged new edition. New York: D. Van Nostrand Company. 1900. 8vo. vii + 414. 664 figs. $2.00 net.

The publication of a second edition of this text-book shows that the clear, concise statements of the essential facts regarding the mineralogical distribution of the principal chemical elements have been well received. In the new, revised, and enlarged edition the crystallography of minerals, according to the chapter on crystallography, has been rewritten to conform to the modern classification of crystals in 32 classes. The presentation is clear and sufficiently full for ordinary courses in colleges and mining schools. Unlike the first edition, the second gives a summary of the optical, thermal, magnetic and electrical characteristics of the different crystal systems.

The second part, dealing with blowpipe analysis, has been revised and somewhat amplified by additions concerning the use of the spectroscope and metallic sodium.

The descriptive mineralogy, forming Part III, presents the minerals grouped according to their most important economic element. The composition, physical features and behavior before the blowpipe are succinctly given and short statements are made regarding the uses of each mineral and the various species with which it may be confused. The selection of minerals for treatment in this part of the volume is, on the whole, in excellent proportion. The differences in economic importance are emphasized by the use of different types. The determinative mineralogy has been entirely rewritten and greatly simplified and the tables have been improved by breaking them up into several smaller groups.

The illustrations of the second edition are a great improvement over the former issue, but the retention of a few cuts of the former style of drawing detracts somewhat from the general tone of the work. E. B. M.

LEHRBUCH DER ANORGANISCHEN CHEMIE (Second Edition). By DR. HUGO ERDMANN, Professor at Halle. Braunschweig: Vieweg und Sohn. 1900. xxvi + 758 pp.

The first edition of this book has already been reviewed in this JOURNAL.[1] The fact that a new edition has appeared in so short a time is evidence that the virtues of the book have made a greater impression than its faults. The second edition contains reference to many new facts which have been discovered since the earlier printing, and gives a somewhat fuller historical treatment in some cases; but, nevertheless, it is essentially unchanged in plan and substance. A careful comparison of the very detailed tables of contents shows the only important alteration in arrangement to have been the questionable shifting of tellurium from its companionship with selenium. It is now to be found among the noble metals, in association with osmium and ruthenium. This adherence to the letter of the periodic table leads one to expect to find more prominence given to this table, even if its spirit is disregarded; but the table is still only to be found in the midst of the singularly cramped confusion of the final chapter.

---

[1] This JOURNAL, 20, 874 (1898).

Many of the earlier misprints have been corrected, and only occasionally does one meet with such a new one as the ascription of "Aetherion" to "Brugh." Among the new facts recorded, the chapter on the noble gases is especially interesting and important, not so much on account of the brilliant chromolithographs of their spectra, as because Professor Ramsay is said to have read the proof.

As before, the weakest side of the book is the lack of unity and clearness in its theoretical framework. Many examples of this deficiency might be cited. For instance, the idea that nitric acid somewhat diluted with water undoubtedly has the formula $N(OH)_5$ is still advanced. The word "phase" does not occur in the index, and does not seem to have been mentioned. Neither does any general reference to the effect of concentration on the direction and progress of a chemical reaction seem to have found a place in the book.

An example of the difference between a veiled and uncomprehending statement and a logical illuminative explanation may be seen on comparing the treatment of the cause of oven-burning plaster of Paris, on p. 529, with that given by Ostwald on p. 531 of the new "Grundlinien"; or on comparing the statements concerning the changing solubility of sodic sulphate, on p. 508, with that given in any modern work on physical chemistry. One cannot but regret that the unusual wealth of material contained in this book should have received so little illumination from modern theory. T. W. R.

QUANTITATIVE CHEMICAL ANALYSIS, Adapted for Use in the Laboratories of Colleges and Schools. BY FRANK CLOWES, D.Sc. (London), and J. BERNARD COLEMAN, A.R.C.Sc. (Dublin). Fifth Edition. Philadelphia: P. Blakiston's Son and Co. 1900. xxiv + 592 pp. Price, $3.50.

This book is offered as a text-book for students, teachers, and others, and is a compendium of general quantitative analysis. The subject-matter has been arranged in seven principal parts, which are subdivided into sixteen sections.

Part I. deals with the preliminary and general operations, such as weighing, determination of specific gravity, preparation of pure substances, and of substances for analysis; Part II. is devoted to simple gravimetric estimations; Part III. treats of volumetric analysis, standard solutions, and calibration of apparatus; Part IV. contains descriptions of more complex gravimetric and volumetric determinations. This section of 217 pages includes the analysis of ores, industrial products, water, food, and organic substances; Part V. treats of gas analysis; Part VI. contains typical results of analyses, tables of constants, specific gravities, and atomic weights; Part VII. gives descriptions of the preparation of gases, use of compressed gases, and the distillation of water. An appendix contains a chapter on some new forms of apparatus, and some recent analytical methods.

By omitting all theoretical considerations, and with the frequent use of cross references, the authors have condensed into 592 pages almost the whole subject of quantitative analysis, and for the most part successfully. When so much material, however, is crowded into such a small space, some of it is sure to suffer. This is particularly true of the more special subjects included in Part IV. The most accurate and most approved methods for the determination of carbon, manganese, and phosphorus in steel are not given. The excellent method of Gibbs for the precipitation of manganese as manganese ammonium phosphate, and the volumetric methods for manganese and phosphorus are not mentioned. The convenient volumetric methods for the determination of fat in milk such as those of Babcock, and Leffmann and Beam are omitted. The subject of electrolytic separations is almost entirely neglected. This is especially so on page 282 where an excellent opportunity presents itself for the electrolytic estimation of copper, lead, and tin in an alloy of those metals.

It is much to be regretted that no references to original articles are given. In the appendix is given a list of text-books for reference, but it would have been much more profitable and useful to have given the authority for many of the processes. It is easy, however, to find fault, and it is not the intention of the reviewer to leave the subject without saying that there is much in the book which is excellent. H. F.

VOL. XXV. APRIL, 1901. No. 4.

AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Case School of Applied Science.

INVESTIGATIONS ON THE COMPOSITION OF PETROLEUM.

BY CHARLES F. MABERY.

XXXV.—ON THE COMPOSITION OF CALIFORNIA PETROLEUM.[1]

BY CHARLES F. MABERY AND EDWARD J. HUDSON.

In its composition as a natural product, California petroleum is the most interesting of any of the numerous petroleums that have come under our observation. When its constituents are more fully understood they will doubtless throw new light on the origin of petroleum, from the fact that they have been subjected to less rigorous agencies during, or subsequent to, their formation than petroleums from other well-known fields. In fields not yet developed, such as those of South America and Japan, similar unstable oils are found. It is useless to attempt to separate from these peculiar oils their individual constituents by the ordinary method of fractional distillation under atmospheric pressure. Not only on account of the high boiling-points, but because the presence of air causes such decomposition, hydrocarbons boiling above

---

[1] Presented to the American Academy of Arts and Sciences, November, 1900. Aid in the work described in these papers was given by the Academy from the C. M. Warren Fund for Original Research.

200° cannot be separated in a pure form without the aid of a vacuum. With no further knowledge of the constituents of the crude oils, this explains the numerous ineffectual attempts during the last thirty years to obtain acceptable refined products from California petroleum. By excluding air, as in vacuum distillation, with the reduction of boiling-points, it is possible to distil without decomposition all the hydrocarbons of the crude oils. With some modifications of the apparatus employed in vacuum distillation of the higher fractions of Pennsylvania oil, the fractional separation may be carried on with little more delay than in distillation under atmospheric pressure. Provision for drawing in fresh fractions without loss of vacuum may be made by sealing on a second tube to the neck of the flask a little lower than the exit tube for the escaping vapors. Then, as in the ordinary application of the Hempel principle, the cooling space in the neck of the flask may be increased by filling it with broken glass. This requires a long-necked flask, and the beads may be supported on a piece of glass rod resting on the bottom of the flask, the upper end flattened so as nearly to fill the neck of the flask as a support to the broken glass. The chief hindrance to the use of beads is the condensation of liquids with high boiling-points in the neck of the flask, due to the cooling effect of the outside air. The neck of the flask must, therefore, be packed an inch or more thick with asbestos. With this arrangement, and with a flat perforated ring burner for heating, the distillation may be conducted with a fairly rapid fractional separation, without decomposition even of the constituents that distil above 350°, 50 mm.

This examination of California oil was undertaken with the intention of ascertaining the series of hydrocarbons which constitute the main body of the crude oil, as well as the principal members of the series, as shown by percentage composition and molecular weights.

The first specimen of crude oil was received through the kindness of Mr. C. A. Black, chemist in an oil company in Ventura County. The second specimen came from a well of the Coalinga Oil Company in Fresno, through the secretary of the company, Mr. Henderson Hayward. These two specimens will be referred to respectively as Ventura oil and Fresno oil. Another specimen was received from the Puente Hills in Los Angeles County, through the kindness of the Puente Oil Company at Chino. This oil will be referred to as Puente oil. Four other specimens were received from the Torrey wells and the "Los Angeles" wells in the Sespe district (Scott's Hill) in Ventura County, through the kindness of the Union Oil Company, at Santa Paula. These samples will be designated respectively as Adams' Cañon, Bardsdale, Scott's Hill, and Torrey oils.

Another specimen is of especial interest, since it came from a well sunk beneath the Pacific Ocean at high tide. It was sent by Mr. J. B. Treadwell from a well at Summerland, Santa Barbara County, at a point where the oil strata outcropped on a north and south line at the top of an elevation, and again descending on the south side, disappeared under the ocean. The well was driven to a depth of 245 feet, just within the shore line at high tide, where it reached the bottom of the oil sand. This oil will be referred to as Santa Barbara oil.

This collection of specimens seemed to offer a fair average of the oils from the California fields, representing four different counties, and deposits that yield oil in considerable quantities.

Since these crude oils differed essentially in their appearance and in their physical properties, in ascertaining their composition it seemed advisable to examine them individually.

In the spring of 1897 an examination of the Ventura oil was begun,[1] and besides giving the composition of the crude oil, the fractional separations were carried far enough *in vacuo* to identify the principal constituents boiling below 175°. The several hydrocarbons homologous with benzene, which have been found in petroleum from other sources, were found to constitute a large part of the unpurified distillates; but the chief constituents were shown by their composition and specific gravity to be methylenes, for the first time recognized as essential constituents of American petroleum.

[1] This JOURNAL, 19, 796 (1897).

PETROLEUM FROM FRESNO COUNTY.

A brief account of the composition of a specimen of crude oil from Fresno County was given in the preliminary paper referred to above. When this oil was subjected to distillation it was evident that decomposition could only be prevented in the fractions above 150° by collecting them *in vacuo.* The portion collected below 150° (atmospheric pressure) —2090 grams—was submitted to long-continued fractional separation within 1° until 50 grams collected below 55°, and only 5 grams between 55° and 68°. At 68° to 70° the distillates amounted to 60 grams, which was separated for the most part at 68°. The specific gravity of the crude distillate at 68° was found to be 0.6913, and, after thorough agitation with fuming sulphuric acid, 0.6844. A combustion of the purified oil gave the following percentages of carbon and hydrogen :

0.1692 gram of the oil gave 0.5234 gram CO_2 ; and 0.2314 gram H_2O.

	Calculated for		
	C_8H_{16}.	C_8H_{18}.	Found.
C	85.70	83.72	84.38
H	14.30	16.28	15.30

The loss in this analysis is doubtless due to an escape of a very small amount of gaseous decomposition-products without complete combustion. Combustion of such a volatile oil requires the closest attention in manipulation to avoid loss in transferring to the combustion tube, and, as will appear later, the highest temperature that the hardest tube will stand is necessary for complete combustion. These results seem to indicate that the oil was a mixture of hexane and hexamethylene. The slight change in specific gravity after treatment with fuming sulphuric acid and potassic hydrate shows that the benzene had been almost completely removed. The fractions at 68° appear to be the last in California oil containing members of the series C_nH_{2n+2}. Since small quantities of distillates collected in the vicinity of 60°, 38°, and in one specimen at 30°, it is probable that the very light gasoline from California oil has the same composition as that from Pennsylvania oil.

The specific gravity of hexane, 0.6630 at 18°, and of hexamethylene, 0.690, also indicate that the fraction 68°–70° is a mixture of these two hydrocarbons.

Heptamethylene, C_7H_{14}.

The distillate collected at 96° to 98° amounted to 50 grams. Before purification, it gave as its specific gravity 0.7499, and after purification 0.7413. The specific gravity of heptane boiling at this point is 0.6440 (20°.5). Beilstein and Kurbatoff gave 0.742 at 18° as the specific gravity of heptanaphthene. A combustion gave the following percentages of carbon and hydrogen:

0.1413 gram of the purified oil gave 0.4442 gram CO_2; and 0.1814 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.74
H	14.30	14.35

A determination of the vapor density of the fraction 96°–98° by collecting the vapor over mercury, gave a value corresponding to the molecular weight of heptamethylene. The determination was made by the method of V. Meyer, *in vacuo*, essentially according to the modification of Lunge and Neuberg:[1]

0.0494 gram of the oil gave 22.9 cc. under a tension of 373 mm. and at 24°.

Calculated for C_7H_{14}.	Found.
3.40	3.40

The high specific gravity of this hydrocarbon corresponding to that of heptanaphthene, the composition given by analysis and the molecular weight, leave no doubt that this body is a heptamethylene, and that heptane is not contained in California (Fresno County) petroleum.

Benzene.

The distillates in the vicinity of 80°, especially at 79° to 81°, gave the characteristic odor of benzene. 20.5 grams of these fractions, shaken below 60° with a mixture of nitric and sulphuric acids, gave a heavy nitro-product; after washing with water and distilling, the distillate weighed 13 grams, showing that 35.5 per cent of this oil was benzene. Some of the same fractions, treated with fuming nitric acid, deposited needle-shaped crystals that melted at 89°–90°, the melting-point of dinitrobenzene.

---

[1] Ber. d. chem. Ges., 1891, 729.

Toluene.

After the twelfth distillation, 60 grams collected at 109°–110° with the penetrating odor of toluene. Thirty grams of this distillate was shaken with a mixture of nitric and sulphuric acids, and the oil not nitrated separated from the nitro-product by distillation. The distillate weighed 13 grams, showing that 54 per cent of the original distillate was toluene. Upon agitating this product with fuming sulphuric acid and distilling, 1.6 per cent more was removed. The remaining oil was dried over sodium for analysis.

The unpurified distillate gave the following values on analysis:

0.1584 gram of the oil gave 0.5090 gram CO_2; and 0.1663 gram H_2O.

	Calculated for		
	Toluene.	C_nH_{2n}.	Found.
C	91.31	85.70	87.64
H	8.69	14.30	11.73

The change in composition by treatment with acids was very marked:

0.1725 gram of the purified oil gave 0.5387 gram CO_2; and 0.2282 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.71

Evidently the small quantity of oil remaining after the treatment with acids was octonaphthene, that had not been completely separated by distillation.

Octonaphthene, C_8H_{16}.

After the twentieth distillation, 30 grams collected at 118°–120°, which, with no further purification than drying over sodium, gave 0.7615 as its specific gravity at 20°, and, on analysis, values required for octonaphthene:

0.1457 gram of the oil gave 0.4566 gram CO_2; and 0.1922 gram H_2O.

C	85.47
H	14.71

After thorough treatment with fuming sulphuric acid the specific gravity was reduced to 0.7532 at 20° (octonaphthene, 0.7582 at 17°.5, Beilstein and Kurbatoff), but the composition was scarcely changed:

I. 0.1471 gram of the oil gave 0.4618 gram CO_2; and 0.1895 gram H_2O.

II. 0.1334 gram of the oil gave 0.4185 gram CO_2; and 0.1762 gram H_2O.

	Calculated for C_nH_{2n}.	Found. I.	II.
C	85.70	85.62	85.54
H	14.30	14.32	14.67

After the eighteenth distillation, 25 grams remained persistently at 124°–125°, which was not affected by fuming sulphuric acid in the cold, but at 100° the acid became colored and gave off much sulphur dioxide. On pouring into water, the solution gave a peculiar odor resembling turpentine, and a black powder separated that contained nitrogen. Analysis of the distillate, after the treatment with the acid, gave values required for C_nH_{2n}:

0.1391 gram of the oil gave 0.4354 gram CO_2; and 0.1875 gram H_2O.

	Required for C_nH_{2n}.	Found.
C	85.70	85.36
H	14.30	14.98

Since no other hydrocarbon than normal octane has been recognized with this boiling-point, this distillate must be a mixture of octonaphthene with a higher body, but evidently normal octane is not present in appreciable quantity.

Nononaphthene, C_9H_{18}.

A considerable quantity of distillate collected at 134°–135°, that gave as its specific gravity 0.8175. After purification with fuming sulphuric acid its specific gravity was reduced to 0.7591. Twenty-eight grams of the crude distillate gave 13 grams of the purified oil with a loss of 53 per cent. The purified oil gave, by the action of fuming nitric acid, a nitro-derivative that, after crystallization from glacial acetic acid, melted at 85°. The melting-point of dinitromesitylene is 86°. A combustion of the purified distillate gave values for carbon and hydrogen required for nononaphthene :

0.1382 gram of the oil gave 0.4318 gram CO_2 ; and 0.1827 gram H_2O.

	Calculated for C_9H_{18}.	Found.
C	85.70	85.21
H	14.30	14.68

Xylenes.

Since para- and metaxylenes have frequently been found in petroleum, it did not seem advisable to separate the isomeric xylenes, although the distillates 137°–140° gave the strong penetrating odor of these bodies. At the end of the thirteenth distillation, 630 grams collected within these limits. On treating 125 grams of this product with a mixture of nitric and sulphuric acids, and agitating below 60°, washing with sodic hydrate and water, drying and distilling, only 50 grams came over below 145°, showing that the xylenes formed 60 per cent of the original distillates and had been removed as nitro-products. At the low temperature of the nitration only the aromatic hydrocarbons could have been affected. The change in composition by the nitration is shown by the following analyses :

0.1469 gram ofthe unpurified oil gave 0.4770 gram CO_2 ; and 0.1495 gram H_2O.

	Calculated for xylene.	Found.
C	92.31	88.53
H	7.69	11.31

Analysis of the purified distillate gave the following results on analysis :

I. 0.1382 gram of the oil gave 0.4318 gram CO_2 ; and 0.1827 gram H_2O.

II. 0.1386 gram of the oil gave 0.4318 gram CO_2; and 0.1837 gram H_2O.

III. 0.1441 gram of the oil gave 0.4492 gram CO_2; and 0.1901 gram H_2O.

	Calculated for C_nH_{2n}.	Found. I.	II.	III.
C	85.70	85.21	84.96	85.00
H	14.30	14.69	14.72	14.66

The chief portion of the nitrated oil was shown to be metaxylene, since the nitro-compound distilled at 240°–260°, and with fuming nitric acid it was converted into a crystalline powder insoluble in alcohol; crystallized from glacial acetic acid, it melted at 176°, the melting-point of trinitrometaxylene. Probably the 50 grams not nitrated was for the most part nononaphthene.

Nonane.

Since considerable quantities of distillates collected in the vicinity of 150°, after the seventeenth distillation, attempts were made to ascertain whether nonane is a constituent of California petroleum. This seemed of especial importance since nonane forms such an important constituent of Pennsylvania petroleum. Without purification a combustion showed the following proportions of carbon and hydrogen: Carbon, 86.14; hydrogen, 12.67. The specific gravity was 0.8117. After agitating several times with fuming sulphuric acid, the composition was materially changed:

0.1719 gram of the oil gave 0.5372 gram CO_2; and 0.2206 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.26

The principal constituent of this fraction was therefore a naphthene, probably hexahydrocumene.

Dekanaphthene, $C_{10}H_{20}$.

At the end of the seventeenth distillation, the quantity of distillates within 1° limits between 159° and 163° amounted to 150 grams. By further distillation these came together for the most part at 160° to 161°. The specific gravity of the unpurified distillate at 20° was 0.8272. When agitated in the cold with fuming sulphuric acid, this distillate developed great heat; after treatment several times, until the acid was no longer much colored, the product was washed with sodic hydrate and water, and dried for analysis. The original distillate lost 75 per cent of its weight by this treatment. The aromatic hydrocarbon doubtless consisted, for the most part at least, of ethyltoluene, boiling-point 161°–162°, but no further attempts were made to identify it.

The specific gravity of the residual oil was 0.7841, practically the same as the specific gravity of dekanaphthene, 0.783, separated by Markownikoff and Oglobin from Baku petroleum. Its odor is precisely similar to that of the corresponding hydrocarbon which one of us (Mabery) has separated from crude Baku oil.

Analysis of the unpurified distillate gave the following values:

I. 0.1462 gram of the oil gave 0.4724 gram CO_2; and 0.1524 gram H_2O.

II. 0.1496 gram of the oil gave 0.4844 gram CO_2; and 0.1564 gram H_2O.

	I.	II.
C	88.10	88.28
H	11.57	11.61

After treatment with the acid the composition was materially changed; the results correspond closely to the composition of dekanaphthene:

0.1481 gram of the oil gave 0.4646 gram CO_2; and 0.1932 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.55
H	14.30	14.50

A determination of the molecular weight gave a value required for dekanaphthene.

0.8850 gram of the oil and 24.22 grams benzene gave, by the Beckmann method, at the freezing-point, a depression of 1°.28.

Calculated for $C_{10}H_{20}$.	Found.
140	140

After the twenty-fourth distillation, 50 grams collected at 169°–170°' which gave as its specific gravity without purification, 0.8358. After thorough agitation with fuming sulphuric acid and washing, the specific gravity was reduced to 0.7749, but the larger portion of the oil was removed by the acid, indicating that the fraction consisted for the most part of a benzene homologue. The small quantity remaining after the treatment was doubtless dekanaphthene, since its specific gravity was nearly the same.

The presence of a naphthene in Russian oil, boiling at 182°, led us to believe that the same body should be found in California oil; but the small quantity of distillate collecting here, only 10 grams after long distillation, excluded this hydrocarbon in any appreciable quantity.

Undekanaphthene, $C_{11}H_{22}$ (195°).

Between 188° and 191°, 50 grams came together at the end of the tenth distillation, which gave the following results on analysis:

0.1423 gram of the oil gave 0.4550 gram CO_2; and 0.1617 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	87.20
H	14.30	12.63

The specific gravity of this distillate before treatment was 0.8386. After vigorous agitation with fuming sulphuric acid, and washing, the specific gravity was reduced to 0.8044.

A distillate separated from Russian oil at 197° gave (Markownikoff and Oglobin) as its specific gravity at 14°, 0.8055, and it was assigned the formula $C_{12}H_{24}$. The quantity of oil remaining after separation of durene, which no doubt was the benzene hydrocarbon in this distillate, was small. That it was a naphthene, as shown by its specific gravity, is confirmed by analysis.

0.1459 gram of the oil gave 0.4575 gram CO_2; and 0.1886 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	85.70	85.70
H	14.30	14.40

Determinations of the molecular weight of this fraction by the Beckmann freezing-point method, using benzene, gave the following value:

0.7901 gram of the oil and 24.68 grams benzene gave a depression of 1°.012.

1.1249 gram of the oil and 25.90 grams benzene gave a depression of 1°.36.

Calculated for $C_{11}H_{22}$.	Found. I.	II.
154	155	157

It appears from these results that the hydrocarbon in California petroleum boiling at 195° is not dodekanaphthene, $C_{12}H_{24}$, but undekanaphthene, $C_{11}H_{22}$. This conclusion is further confirmed, as will appear later, by the composition of the distillate 216°, which appears to be dodekanaphthene, and still further by the composition of the monochlornaphthene obtained from the hydrocarbon boiling at 195° which gives as its formula $C_{11}H_{21}Cl$.

In the vicinity of 200°, 50 grams of a distillate collected which gave as its specific gravity 0.8684. After agitation with fuming sulphuric acid, the specific gravity was diminished to 0.8202. An analysis before treatment gave 87.84 per cent of carbon and 11.91 per cent of hydrogen. After treatment with the acid, the analysis gave 85.99 per cent of carbon and 13.97 per cent of hydrogen, showing that some of the aromatic hydrocarbon still remained; the small amount of naphthene was doubtless undekanaphthene, boiling at 195°; sp. gr. 0.8010, as given above.

Dodekanaphthene, $C_{12}H_{24}$.

A considerable quantity of distillate collected at 208° to 210°, corresponding to 216°, which corresponded in composition by analysis and molecular weight to dodekanaphthene:

0.1496 gram of the oil gave 0.4677 gram CO_2; and 0.1962 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.26
H	14.30	14.57

Determinations of the molecular weight of this product by the Beckmann method at the freezing-point, gave results corresponding to the formula of dodekanaphthene.

1.0141 grams of the oil and 25.61 grams benzene gave a depression of 1°.17.

Calculated for $C_{12}H_{24}$.	Found.
166	166

It is therefore evident that California petroleum differs from Russian oil in containing dodekanaphthene, boiling at 216°, as well as undekanaphthene, boiling at 195°.

Puente Oil.

The specimen received from the Puente Oil Company was somewhat thicker than the Fresno oil. Its specific gravity at 20° was found to be 0.892. It contained 0.80 per cent of sulphur. Two determinations of nitrogen by the Kjeldahl method gave: (I) 0.564, (II) 0.587; and by the absolute method, measuring the volume of nitrogen, (I) 1.18, and (II) 1.22. A combustion of the crude oil gave 84.96 per cent of carbon and 11.96 per cent of hydrogen. Two determinations of bromine absorption gave: (I) 18.8, and (II) 18.3 per cent.

A distillation of 1346 grams of the crude oil, under atmospheric pressure, gave the following weights:

Below 100°.	100°–150°.	150°–200°.	200°–250°.
167	170	132	130 grams

The small proportions distilling below 250° made it evident that the chief constituents could only be separated *in vacuo*. The specific gravity of these distillates at 20° were ascertained by weighing on a Westphal balance:

100°.	100°–150°.	150°–206°.
0.7642	0.8155	0.8538

Ten liters of the Puente crude oil, after collecting below 150° at atmospheric pressure, gave the following weights under 50 mm:

150 at. pr.	Below 120°.	120°–150°.	150°–175°.	175°–185°.	185°–200°.
590	800	827	990	160	495 grams

The residue above 200° was next divided into fractions of convenient size, without noting temperatures:

1.	2.	3.	4.
655	1010	670	430 grams

Further distillation of the fraction –150 atmospheric pressure gave the following weights :

Below 60°.	60–62°.	66°–68°.	78°–82°.	88°–90°.	96°–98°.	109°–110°.	118°–120°.
10	10	10	27	40	120	60	65 grams

Smaller weights collected at intermediate temperatures.

Heptamethylene, C_7H_{14}.

No attempts were made to ascertain the composition of the individual fractions below 96° from Puente oil. Those portions will receive further attention with the corresponding distillates from the other oils. Without purification the distillate 96°–98° gave as its specific gravity at 20°, 0.7499. After repeated agitation with fuming sulphuric acid and potassic hydrate the specific gravity was scarcely changed, 0.7440; specific gravity of heptanaphthene, 0.742 at 18°. Analysis I. was made of the untreated oil, Analysis II. of the portion after treatment :

I. 0.1409 gram of the oil gave 0.4438 gram CO_2 ; and 0.1683 gram H_2O.

II. 0.1396 gram of the oil gave 0.4383 gram CO_2; and 0.1792 gram H_2O.

	Calculated for C_7H_{14}.	Found. I.	II.
C	85.70	85.90	85.60
H	14.30	13.27	14.26

The difference in Analysis I. is doubtless due to oxygen and nitrogen compounds, since agitation of the crude distillates with potassic hydrate separates from most of the distillates from California petroleum heavy oils, with an odor resembling that of creosote. A description of these oxygenated compounds is reserved for a later paper. The specific gravity of the purified fraction, 0.7440, is essentially the same as that of heptanaphthene separated from Russian oil, 0.748, by Beilstein and Kurbatoff.

Octonaphthene, C_8H_{16}.

The fraction 118°–120°, without further treatment, gave as its specific gravity at 20°, 0.7615, which was reduced to 0.7540 by agitation with fuming sulphuric acid. Specific gravity of octonaphthene, 0.7552 at 17°.5. Analysis I. was made of the crude distillate, and Analysis II. of the oil after purification with the acid:

I. 0.1406 gram of the oil gave 0.4424 gram CO_2; and 0.1760 gram H_2O.

II. 0.1503 gram of the oil gave 0.4692 gram CO_2; and 0.1941 gram H_2O.

	Calculated for C_8H_{16}.	Found. I.	Found. II.
C	85.70	85.81	85.20
H	14.30	13.91	14.35

No further examination was made of the fractions from 120° to 140°, but it seemed of interest to ascertain whether nonane formed any part of the distillate 148°–150°, since it forms such a large proportion of the Eastern oils. The crude distillate 150°–151° gave as its specific gravity 0.7910, and after purification with sulphuric acid, 0.7730. Analysis of the treated oil gave percentages of carbon and hydrogen that still showed the presence of the benzene homologue.

0.1449 gram of the oil gave 0.4589 gram CO_2; and 0.1807 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	86.37
H	14.30	13.57

From the results of this analysis it is evident that nonane forms no appreciable proportion of Puente oil.

Dekanaphthene, $C_{10}H_{20}$.

Fifty grams of a distillate collected at 160°–162°, with smaller quantities on either side. A determination of its specific gravity at 20° gave 0.7966, and after agitation with sulphuric acid, 0.7745. The composition of this distillate after treatment with the acid was shown by analysis:

0.1747 gram of the oil gave 0.5515 gram CO_2; and 0.2185 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	86.09
H	14.30	13.90

Fraction 168°–172°.

In all the California oils examined, as stated above, considerable quantities have collected at 168°–172°. Since large proportions of the benzene hydrocarbons appear in all these oils, the distillate 168°–172° might exist to a large extent of pseudocumene, boiling-point 168°. The high specific gravity of the fraction before treatment with the acid, 0.8063, and the lower value after treatment, 0.7874, indicates a considerable proportion of the benzene homologue. Even after the acid treatment, the percentages of carbon and hydrogen showed the presence still of the same constituent: carbon, 85.91; hydrogen, 13.61. It seems probable, therefore, that the benzene homologue constitutes the greater part of this distillate, and the residue, after treatment, is doubtless higher or lower constituents; but the absence of a decane corresponding to the decane in Pennsylvania petroleum, boiling at 172°, is assured.

Fraction 180°–182°.

Only 10 grams collected at 180°–182°, with smaller quantities on either side. Although this quantity of the oil was insufficient for complete examination, its specific gravity before and after analysis was ascertained, and an analysis made after treatment with acid. Before treatment the value obtained was 0.8116, and afterward 0.7955. A combustion gave 86.27 per cent of carbon, and 13.79 per cent of hydrogen. Evidently, like the Fresno oil, Puente oil has no constituent with this boiling-point, except a benzene homologue.

Undekanaphthene, $C_{11}H_{22}$ (195°).

A naphthene should be expected between 190° and 200°, since undekanaphthene, $C_{11}H_{22}$, is a constituent of the Fresno oil. The 20 grams collecting at 190°–192° gave as its specific gravity at 20°, 0.8196, and after treatment with fuming acid, 0.8046 (0.8055 at 14°, Markownikoff). A combustion of the oil after treatment gave 85.90 per cent of carbon and 13.85 per cent of hydrogen.

The series C_nH_{2n+2} forms no part of the Puente oil, at least above 95°. The low percentage of hydrogen seems to indicate a series still poorer in hydrogen than the naphthenes, especially in the higher distillates, possibly a series C_nH_{2n-2}, containing two naphthene rings. Whether such hydrocarbons are really present, or whether benzene homologues have not been completely removed, will appear in more prolonged distillation of these oils boiling above 200°.

BARDSDALE OIL.

The specimen marked "Owens No. 2," sent by the Union Oil Co. from the Bardsdale district, was quite thick and heavy. Its specific gravity at 20° was 0.8923. It contained 1.25 per cent of nitrogen, as shown by the volume of nitrogen collected. A Kjeldahl determination gave 0.50 per cent. A Carius determination gave 1.5 per cent of sulphur, showing it to be a high sulphur oil. A combustion gave 84.17 per cent of carbon and 12.15 per cent of hydrogen. 108 grams of the oil distilled under atmospheric pressure gave the following weights:

Below 150°.	150°–310°.	310°–410°.
9	24	7 grams
0.7433	0.8170	Specific gravity

In distilling 5088 grams under 50 mm., except –150°, the following weights were obtained:

Below 150° at. pr.	150°–200°.	200°–250°.	250°–290°.
250	555	374	1165 grams

The two fractions below 200° were distilled within 5°, and then within 2°, which brought together the following weights with smaller quantities at neighboring temperatures:

96°–100°.	116°–120°.	136°–140°.	148°–150°.	158°–162°.	168°–172°.	190°–194°.
34	25	35	40	60	20	40 grams

The lower portions of this oil began to come over at 45°, but only small quantities collected below 65°. At 65°–70°, 40 grams collected, which will be examined in connection with the similar distillates from the other oils to ascertain whether the principal constituent is hexane or hexamethylene. The high specific gravity of this oil, even after treating thoroughly with fuming sulphuric acid, 0.7017, would seem to exclude hexane, sp. gr. 0.6671.

Heptamethylene, C_7H_{14}.

The unpurified fraction, 96°–100°, gave as its specific gravity at 20°, 0.7395, and after treatment with fuming acid, 0.7384. The slight change in specific gravity indicates that this fraction consists for the most part of one hydrocarbon, and analysis with the boiling-point shows that the hydrocarbon is heptamethylene, sp. gr. 0.7420.

0.1473 gram of the oil gave 0.4620 gram CO_2; and 0.1879 gram H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.54
H	14.30	14.18

Octonaphthene, C_8H_{16}.

The specific gravity of the fraction 116°–120° was 0.7625, and after treatment with fuming sulphuric acid, 0.7566, which indicated that this product contained very little of the benzene homologues. An analysis, after purification, gave proportions of carbon and hydrogen required for octonaphthene:

0.1780 gram of the oil gave 0.5572 gram CO_2; and 0.2287 gram H_2O.

	Calculated for C_8H_{16}.	Found.
C	85.70	85.39
H	14.30	14.28

Fraction 150°–152°.

The distillates above 120° received no further attention, except to ascertain that the xylols were present in large proportion, as in the other oils. To ascertain whether nonane is contained in this oil, the specific gravity of the fraction 150°–152° was ascertained and found to be 0.7756, after treatment with the fuming acid. Its composition, after treatment with the acid, corresponded to that of C_nH_{2n}:

0.1434 gram of the oil gave 0.4480 gram CO_2; and 0.1839 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.25

The lower specfic gravity of nonane and the results of analysis show that nonane is not a constituent of this oil.

Dekanaphthene, $C_{10}H_{20}$.

The specific gravity of the unpurified fraction 160°–162° at 20° was 0.7966, and after purification with fuming sulphuric acid and sodic hydrate was 0.7905 ($C_{10}H_{20}$, 0.7950 at 0°, Markownikoff).

It gave the following results on analysis:

I. 0.1471 gram of the oil gave 0.4625 gram CO_2; and 0.1907 gram H_2O.

II. 0.1475 gram of the oil gave 0.4477 gram CO_2; and 0.1813 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found. I.	Found. II.
C	85.70	85.50	85.86
H	14.30	14.37	14.17

On account of the small amount of the distillate 167°–170°, no examination was made of it. It was doubtless chiefly a benzene homologue.

Fraction 176°–178°.

To ascertain whether a naphthene boiling at 182° is present in this oil, the fraction 176°–178° was treated thoroughly with fuming sulphuric acid and sodic hydrate. Its specific gravity before treatment was 0.8116; after treatment, 0.7955. It gave, on analysis, 86.01 per cent carbon and 13.31 per cent hydrogen, indicating still the presence of a benzene homologue. But the small quantity remaining showed the absence of any other constituents with this boiling-point in this distillate.

Undekanapthene, $C_{11}H_{22}$.

The fraction 190°–194° gave 0.8186 as its specific gravity before treatment with fuming sulphuric acid and sodic hydrate, and afterward 0.8046. Markownikoff found 0.8119 at 0° as the specific gravity of dodekanaphthene from Baku oil.

The percentages of carbon and hydrogen given by analysis supported the formula of undekanaphthene:

0.1466 gram of the oil gave 0.4588 gram CO_2; and 0.1909 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	85.37
H	14.30	14.47

Some of the Bardsdale distillates, 140°–220°, 50 mm., turned pink soon after they were collected, changing to a darker red on standing, and after some time they deposited a dark oil. The colored distillates alternated with the others, leaving sharply-lined uncolored oils besides those depositing the insoluble heavy oils. The following distillates were colored:

154°–156°, 158°–160°, 168°–170°, 180°–182°, 198°–206°, 212°–216°.

The distillates between these were nearly or quite colorless. This coloration was caused by the phenol bodies, which are easily extracted by alkaline hydrates. The bodies will receive further attention in another paper.

ADAMS CAÑON OIL.

The Adams Cañon Oil from the Ex-Mission district was thicker and heavier than the oils previously described. The specific gravity of this specimen at 30° was 0.9212. It contained a large percentage of nitrogen, 1.46, determined by the volume of nitrogen. The Kjeldahl method gave 0.58 per cent. Two determinations of sulphur gave: (I) 0.92; (II) 0.87. This oil contained a very small proportion of the lower hydrocarbons. 100 grams distilled under atmospheric pressure gave 8 grams below 150°, and 27 grams, 150°–300°. The specific gravity of the lower distillate was 0.7673, and of the higher 0.8457. In vacuum distillation, 9382 grams of the crude oil gave the following weights:

Below 150° at. pr.	–120°.	120°–160°.	160°–250°.
123	865	1045	525

Nearly three-fourths of the original oil remained above 250°.

Continuing the distillation of the lower distillates within 5° and 2°, the following weights were collected:

96°-100°.	116°-120°.	158°-160°.	168°-170°.	180°-182°.
37	10	12	20	10 grams

In continuing the distillation of the lower fractions nothing came over below 60°, and only in quantities of a few grams below 95°.

Heptamethylene, C_7H_{14}.

The fraction 98°–100° unpurified gave as its specific gravity at 20°, 0.7444, and after treatment with fuming sulphuric acid and sodic hydrate, 0.7414. A combustion of the purified oil gave the following percentages of carbon and hydrogen:

0.1525 gram of the oil gave 0.4797 gram CO_2; and 0.1976 gram H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.53
H	14.30	14.40

As in the other oils, much benzene was contained in the fractions near 80°, and toluene in those near 110°.

Octonaphthene, C_8H_{16}.

The fraction 118°–120° gave as its specific gravity unpurified at 20°, 0.7632, and after treatment with fuming acid and sodic hydrate, 0.7600. Specific gravity of octonaphthene, 0.7582. This distillate gave, after purification, 86.52 per cent of carbon, and 14.60 per cent of hydrogen, which with its boiling-point showed it to be octonaphthene.

To ascertain whether nonane is a constituent of Adams Cañon oil, the specific gravity of the distillate 148°–150° was determined, and found to be 0.7858. After treatment with the fuming acid and sodic hydrate its specific gravity was but slightly changed, 0.7800. A combustion then gave 86.10 per cent of carbon and 13.91 per cent of hydrogen.

Since nonane requires 84.37 per cent of carbon and 15.63 per cent of hydrogen, it is evident that this hydrocarbon is not a constituent of Adams Cañon oil.

Dekanaphthene, $C_{10}H_{20}$.

The unpurified distillate 158°–160° gave as its specific gravity at 20°, 0.7972, and 0.7904 after treatment with the fuming acid and sodic hydrate. A combustion of the purified oil gave the following percentages of carbon and hydrogen:

0.1455 gram of the oil gave 0.4583 gram CO_2; and 0.1804 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.91
H	14.30	13.78

The low percentage of hydrogen and high percentage of carbon indicates that the benzene homologue was not completely removed. In some of these distillates the benzene hydrocarbon is present in such large proportion that long continued action of the fuming acid is necessary to remove it completely.

The small amount of the distillate 180°–182° gave as its specific gravity, at 20°, 0.8154, and after treatment with the fuming acid, 0.8097. A combustion of the treated oil gave 85.56 per cent of carbon and 13.95 per cent of hydrogen. No further examination was made of the fractions collected under atmospheric pressure. Like the Bardsdale oil, part of the distillates between 140° and 220° under 50 mm. turned pink soon after they were collected, and on standing deposited a dark colored oil.

While the possibility of hydrocarbons poorer in hydrogen, such as condensed naphthenes, is suggested by the low percentage of hydrogen, on account of the very large proportion of aromatic derivatives of benzene contained in Adams' Cañon oil, it seems more probable that these results are due to benzene derivatives not wholly removed, especially as the boiling-points of the double-ring naphthenes undoubtedly are much higher. Such a double-ring naphthene, apparently formed as one of the products by the action of sodium on monochlorheptamethylene boiled in the vicinity of 240°.

TORREY WELLS OIL.

The specimen of petroleum from the Torrey wells was much lighter than that from Adams Cañon; its specific gravity, at 20°, was 0.8837. It contained 0.49 per cent of sulphur, and gave 0.38 per cent of nitrogen by the Kjeldahl method and 1.15 per cent by volume. A combustion gave 86.00 per cent of carbon and 12.48 per cent of hydrogen; 100 grams distilled under atmospheric pressure gave 11 grams with a specific gravity of 0.7519 below 150° and 29 grams, sp. gr. 0.8226, between 150° and 250°. In distilling Torrey oil *in vacuo*, 9860 grams gave the following weights:

Below 160° at. pr.	–125°.	125°–175°.	175°–225°.	225°–275°.
655	790	1175	900	700 grams

Further distillation of the lower fractions gave, after the fourth distillation, the following weights, with smaller proportions at temperatures between:

96°–98°.	116°–120°.	136°–140°.	158°–162°.	168°–171°.	178°–182°.
78	40	45	37	43	35 grams

The Torrey oil contained more of the lower distillates than any other of the specimens examined. Several grams collected below 40°, and at 65° to 70°, 30 grams came together. The unpurified distillate 65°–70° gave as its specific gravity, at 50° 0.6981, which was reduced only to 0.6926 after agitation with fuming sulphuric acid. The specific gravity of hexane, boiling at 68°, is 0.6630.

Analysis of the purified oil gave the following results:

I. 0.1551 gram of the oil gave 0.4768 gram CO_2; and 0.2138 gram H_2O.

II. 0.1995 gram of the oil gave 0.6146 gram CO_2; and 0.2769 gram H_2O.

III. 0.1369 gram of the oil gave 0.4248 gram CO_2; and 0.1888 gram H_2O.

	Calculated for		Found.		
	C_6H_{12}.	C_6H_{14}.	I.	II.	III.
C	85.70	83.72	83.85	83.93	84.63
H	14.30	16.28	15.32	15.41	15.33

In Analysis III. every precaution was taken to avoid loss of the oil after weighing, and the temperature of the combustion was maintained as high as the tube would stand. Probably the coincidence in the percentages of hydrogen is due to retention of unsaturated hydrocarbons in the sulphuric acid.

Apparently, as in the Fresno oil, the hydrocarbon at 68° is a mixture of hexane and hexamethylene.

Heptamethylene, C_7H_{14}.

The fraction 96°–98° had the specific gravity, at 20°, 0.7496, which was scarcely changed by treatment with fuming sulphuric acid, 0.7430. Analysis I. was made of the crude distillate, and Analysis II. of the purified product:

I. 0.1222 gram of the oil gave 0.3810 gram CO_2; and 0.1602 gram H_2O.

II. 0.1530 gram of the oil gave 0.4801 gram CO_2; and 0.1974 gram H_2O.

	Calculated for C_7H_{14}.	Found. I.	II.
C	85.70	84.97	85.60
H	14.30	14.56	14.34

This product is, therefore, fairly pure heptamethylene.

The fractions in the vicinity of 110° were shown to be composed for the most part of toluene by the formation of nitro-products.

Octonaphthene, C_8H_{16}.

The specific gravity of the crude distillate 118°–120° was 0.7598, and after purification with fuming sulphuric acid and sodic hydrate, 0.7530. A combustion of the unpurified oil gave 86.21 per cent of carbon and 13.35 per cent of hydrogen.

A combustion, after purification, indicated octonaphthene, although the percentage of hydrogen is somewhat too high, probably on account of accidental moisture :

0.1470 gram of the oil gave 0.4598 gram CO_2; and 0.1976 gram H_2O.

	Calculated for C_8H_{16}.	Found.
C	85.70	85.34
H	14.30	14.93

The distillates 135°–140° consisted largely of the xylenes.

Dekanaphthene, $C_{10}H_{20}$.

The specific gravity of the crude fraction 158°–160° was 0.7742, and after purification with the fuming acid and sodic hydrate, 0.7742. Carbon and hydrogen were determined in the purified oil :

0.1455 gram of the oil gave 0.4583 gram CO_2 ; and 0.1804 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.91
H	14.30	13.78

Determinations of the specific gravity of the crude distillate 168°–170 gave 0.7928, and 0.7840 after treatment with fuming acid and sodic hydrate. A combustion of the purified oil gave 85.98 per cent of carbon and 13.69 per cent of hydrogen.

The fraction 178°–182° had the specific gravity before treatment, 0.8006, and afterward, 0.7924. A combustion of the oil after treatment gave 85.97 per cent of carbon and 13.51 per cent of hydrogen. The fraction 198°–200° had the specific gravity of 0.8133, and after treatment 0.8069. The following percentages were given by combustion: carbon, 86.51; hydrogen, 13.54.

The low proportions of hydrogen and high proportions of carbon alluded to before are especially apparent in the Torrey oil. Whether this be due to a higher series or to benzene homologues not easily removed will appear later in the composition of the higher vacuum distillates.

The Torrey distillates 140°–220°, 50 mm., showed a larger proportion of oxygen and nitrogen compounds than any other of the crude oils.

SCOTT'S HILL (SESPE DISTRICT) OIL.

The specimen of petroleum from Scott's Hill was lighter than the Torrey oil; its specific gravity at 20°, was 0.8782. It contained 1.25 per cent of nitrogen. Two determinations of sulphur gave (I) 0.38 and (II) 0.49 per cent. 8260 grams of the crude oil gave the following weights on distillation *in vacuo*:

Below 150° at. pr.	–160°.	160°–208°.	208°–275°.
1220	495	930	880

The distillate –150° was collected under atmospheric pressure, the others under 70 mm. The portion –150° was subjected to further distillation collecting at first within 5°, and twice within 2°. The fractions collected in larger quantities within the following limits:

66°–70°.	86°–90°.	96°–100°.	116°–120°.	136°–140°.	156°–160°.	170°–174°.	178°–182°.	190°–192°.
26	38	35	37	38	62	41	38	41

Continuing the distillation of the higher fractions *in vacuo*, after the third distillation within limits of 2°, the larger quantities collected within the following limits with smaller quanties between:

144°–148°.	164°–168°.	182°–186°.	210°–214°.
60	55	65	23

In distilling corresponding fractions from other fields *in vacuo* a tendency to collect within the same limits was observed. After agitation with fuming sulphuric acid, the fraction 66°–70°, atmospheric pressure, gave as its specific gravity, at 20°, 0.6984; a value much higher than the specific gravity of hexane, 0.6630 (17°.5). A combustion gave percentages of carbon and hydrogen corresponding to a mixture of hexamethylene and hexane:

	Calculated for		
	C_6H_{12}.	C_6H_{14}.	Found.
C	85.70	83.72	84.67
H	14.30	16.28	15.15

The distillates 65°–70° from Torrey, Scott's Hill, and Fresno oils were put together and carefully distilled a number of times in order to separate, so far as possible, the hydrocarbon boiling at 68° or 69° from other admixtures, and the fraction 68°–69° was thoroughly treated with fuming sulphuric acid, warming gently, and allowing it to stand with the acid over night. Before treatment the specific gravity, at 20°, was 0.7005, and after treatment 0.6929. The following results were obtained by analysis:

0.2422 gram of the oil gave 0.7596 gram CO_2; and 0.3234 gram H_2O.

	Calculated for		
	C_6H_{12}.	C_6H_{14}.	Found.
C	85.70	83.72	85.50
H	14.30	16.28	14.84

In this analysis the combustion tube was filled with oxygen before the oil was volatilized, and the temperature was kept as high as the tube would stand.[1] There seems, therefore, to be little doubt that the hydrocarbon in California petroleum boiling at 68°–69° is composed chiefly of hexamethylene.

---

[1] In a paper on the determination of carbon and hydrogen by combustion, using copper oxide (J. Am. Chem. Soc., April, 1900), I mentioned as one of the essential details that the combustion tube must be heated as hot as it would stand. I have observed invariably, in the analysis even of perfectly pure substances, with the tube heated to redness, that the percentages of carbon and hydrogen came too low. I ascribed this loss to the formation of marsh gas which could not be completely burned at temperatures lower than a dull white heat. In a recent investigation on the temperatures of combustion of hydrogen and marsh gas by passing over heated copper oxide, Armand Gautier (Compt. rend. (1900), 130, (1353–1360), finds that hydrogen is completely oxidized by heating just to redness in a length of oxide less than that of a combustion tube. But methane largely diluted with air, 16 methane to 100,000 air, is only partly burned, 58.3 per cent hydrogen in the methane and 36 per cent of the carbon only were oxidized. Even in a much longer tube methane was not completely oxidized. This agrees with my experience, since with temperatures below very bright redness, even in a tube five feet long, the combustion was incomplete.—C. F. M.

Since small quantities of distillates remained in the vicinity of 90° to 91°, it suggested the possibility that isoheptane might form a part of this product. But its high specific gravity, 0.7303 at 20°, isoheptane 0.6819 (17°.5), and the composition showed by analysis excluded isoheptane in any considerable quantity.

0.1273 gram of the oil gave 0.3987 gram CO_2; and 0.1665 gram H_2O.

	Calculated for C_7H_{14}.	Calculated for C_7H_{16}.	Found.
C	85.70	84.00	85.40
H	14.30	16.00	14.53

Special precautions were taken in this analysis to have the temperature of the combustion as hot as possible, and the tube was filled with oxygen before the oil volatilized. The proportions of carbon and hydrogen indicating the absence of isoheptane could not have been due to the presence of benzene, since the oil was treated several times with fuming sulphuric acid. The volatile portions of California petroleum, therefore, contain at most very small proportions of the hydrocarbons, C_nH_{2n+2}, and these, if present, consist almost exclusively of members below normal hexane. Further confirmation of these formulæ is given by the chloride derivatives, which will be described in another paper.

Heptamethylene, C_7H_{14}.

The fraction 96°–98° gave as its specific gravity, at 20°, 0.7479, and after purification with fuming sulphuric acid, 0.7436. A combustion of the purified oil gave the following results:

0.1530 gram of the oil gave 0.4801 gram CO_2; and 0.1974 gram H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.60
H	14.30	14.34

These values leave no doubt that this constituent was heptamethylene.

Octonaphthene, C_8H_{16}.

A determination of the specific gravity of the fraction 118°–120°, at 20° gave 0.7628, and after agitation with fuming acid and sodic hydrate, 0.7569. Determinations of carbon and hydrogen were made both before and after purification.

I. 0.1644 gram of the unpurified oil gave 0.5196 gram CO_2; and 0.1975 gram H_2O.

II. 0.1470 gram of the purified oil gave 0.4600 gram CO_2; and 0.1976 gram H_2O.

	Calculated for C_8H_{16}.	Found. I.	Found. II.
C	85.70	86.21	85.34
H	14.30	13.35	14.93

Although all these oils were dried over sodium, the hydrogen in Analysis II. is somewhat too high, probably on account of a trace of moisture.

No further examination of the higher fractions of this oil below 160° was made, except of the portion collected at 135° to 140°, to show that large proportions of the xylenes were contained as in the other specimens examined.

Dekanaphthene, $C_{10}H_{20}$.

The specific gravity of the fraction 158°–160° was found to be 0.7848, and after agitation with the fuming acid, 0.7751. The proportions of carbon and hydrogen were determined by analysis:

I. 0.1444 gram of the oil gave 0.4575 gram CO_2; and 0.1885 gram H_2O.

II. 0.1451 gram of the oil gave 0.4533 gram CO_2; and 0.1848 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found. I.	Found. II.
C	85.70	85.65	85.24
H	14.30	14.22	14.33

Undekanaphthene, $C_{11}H_{22}$.

The specific gravity of this fraction, without purification, was 0.8093 at 20°, and after treatment with the fuming acid and sodic hydrate, 0.7952. A combustion gave the following percentages of carbon and hydrogen:

0.1458 gram of the oil gave 0.4593 gram CO_2; and 0.1817 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	85.90
H	14.30	13.85

Assuming, which is probable, that the benzene homologue was completely removed, these proportions of carbon and hydrogen point to the presence of a hydrocarbon of a series containing less hydrogen.

A similar result was obtained with the fraction 194°–196°, specific gravity crude, 0.8145; and after treatment, 0.8022. Combustion of the purified oil gave the following percentages:

	I.	II.
C	85.52	85.85
H	13.97	13.92

While the percentages of carbon in these analyses are satisfactory for the formula C_nH_{2n}, the percentages of hydrogen are less satisfactory. The deficiency of about 0.5 per cent in the sum of the carbon and the hydrogen has appeared in many of the analyses of products that could be reasonably accepted as to their formulas. With the greatest care in the details of analysis, we have also found difficulty in obtaining the total carbonic dioxide evolved by combustion of the oil in the ordinary method of analysis. This subject has received attention in another paper on this method of analysis.

Tridekanaphthene, $C_{13}H_{26}$.

After the separation of distillates *in vacuo* from the crude oils, the fractions may be distilled at temperatures which would cause decomposition of constituents of the crude oil. It is therefore possible to continue the distillation of the hydrocarbons even as high as tridekanaphthene under atmospheric pressure after the first distillation. In continuing the distillation, 35 grams collected at 230°–232°, sp. gr. 0.8511. After purification with fuming sulphuric acid it gave as its sp. gr. 0.8134 at 20°. A combustion gave the following results:

0.1511 gram of the oil gave 0.4733 gram CO_2; and 0.1937 gram H_2O.

	Calculated for $C_{13}H_{26}$.	Found.
C	85.70	85.41
H	14.30	14.24

This formula was also verified by a determination of its molecular weight:

1.2712 grams of the oil and 25.24 grams benzene gave a depression of 1°.370.

Calculated for $C_{13}H_{26}$.	Found.
182	180

A determination of the index of refraction gave 1.4745, and the molecular refraction 60.254; calculated for $C_{13}H_{26}$, 59.839.

Tetradekanaphthene, $C_{14}H_{28}$.

A considerable quantity of distillate collected at 144° to 146°, which gave as its specific gravity before purification 0.8428, and after purification 0.8154. A combustion gave percentages of carbon and hydrogen required for the formula C_nH_{2n}.

0.1462 gram of the oil gave 0.4600 gram CO_2; and 0.1824 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.81
H	14.30	13.87

A determination of molecular weight at the freezing-point gave a value required for tetradekanaphthene:

1.3356 gram of the oil and 24.22 grams benzene gave a depression of 1°.394.

Calculated for $C_{14}H_{28}$.	Found.
196	194

The index of refraction of this hydrocarbon was found to be 1.4423, and the molecular refraction, 63.75; required for $C_{14}H_{28}$, 64.44.

Pentadekanaphthene, $C_{15}H_{30}$.

From each of the California oils, distillates *in vacuo* collected at 160°–162°, 50 mm., corresponding nearly to 260° to 262°, atmospheric pressure. The specific gravity of the fraction from Scott's Hill oil was 0.8600, and after purification with fuming sulphuric acid, 0.8171. A combustion gave the following values for carbon and hydrogen :

0.1454 gram of the oil gave 0.4558 gram CO_2 ; and 0.1829 gram H_2O.

	Calculated for $C_{15}H_{30}$.	Found.
C	85.70	85.47
H	14.30	13.97

The percentages of carbon and hydrogen in the analysis of the two hydrocarbons last described indicate a falling off in the proportions of hydrogen. The deficiency in the analysis is more probably due to loss of carbonic dioxide than of water. Similar variations have been noted in connection with some of the lower hydrocarbons in other crude California oils. The deficiency in hydrogen may indicate, as mentioned heretofore, the presence of hydrocarbons composed with more than one methylene ring, which would require prolonged distillation for their complete removal. From the heavier California oils composed, it appears, largely of asphaltic hydrocarbons, the falling off in the proportion of hydrogen and consequent increase in carbon indicates the presence of hydrocarbons with the formula C_nH_{2n-2}. Such differences do not appear in determinations of molecular weights, but are shown by analysis.

There are wide variations in the specific gravity of the distillates of California oil above 230° from different sources. This may indicate a certain proportion of hydrocarbons of a lower series than C_nH_{2n}, and the higher percentages of carbon and lower percentages of hydrogen in some of these oils indicate the possibility of hydrocarbons C_nH_{2n-2}.

For faithful assistance in this work, the following gentlemen should receive credit: Messrs. Shaw, Ames, Richards, Cushing.

From this examination of California petroleum, the following conclusions may be drawn :

An essential characteristic is the relatively small proportions of the distillates below 225°. The main body of the crude oils from the principal fields distilling below 225° is composed of methylenes which resemble those identified in Russian oil, in boiling-points, and in specific gravity, except undekanaphthene, $C_{11}H_{22}$, dodekanaphthene, $C_{12}H_{24}$, and tridekanaphthene, $C_{13}H_{26}$, which differ in boiling-points. The proportion of the aromatic hydrocarbons is much larger, apparently, in California oil. The homologues of benzene form a considerable proportion of the distillates, especially of those with lower boiling-points. In the distillate 221°–222° from Puente oil so much naphthalene was present that the distillate became solid at 0°.

California petroleum differs totally from the Eastern oils—Pennsylvania, Ohio, Canadian, etc.—and also materially from Russian oil, in not containing members of the series C_nH_{2n+2}. In this respect, and in respect to the large proportion of aromatic hydrocarbons, California petroleum is unlike any other petroleum that has been examined in this laboratory. Incidentally it may be mentioned that California petroleum differs from other petroleums hitherto examined in the large proportions of oxygen and nitrogen compounds which it contains. These bodies are under investigation in this laboratory.

Study of the portions with high boiling-points, which is now in progress, will have an especial interest, since, when they are separated without decomposition, they form the most valuable constituents of lubricating oils and asphalts that have been separated from petroleum. In some of the high distillates, such as those from Summerland oil, hydrocarbons of the series C_nH_{2n-2} and the series C_nH_{2n-4} have been identified.

XXXVI.—ON THE CHLORINE DERIVATIVES OF THE HYDROCARBONS IN CALIFORNIA PETROLEUM.

BY CHARLES F. MABERY AND OTTO J. SIEPLEIN.

In further confirmation of the composition of the hydrocarbon 68°–70°. described in the previous paper (Mabery and Hudson), the chlorine derivatives were formed by exposing the hydrocarbon over water to the action of chlorine, in ordinary daylight. After washing and drying, the chlorine product was fractioned under atmospheric pressure until it collected at 125° to 130°, and for the most part at 126°. It distilled under normal conditions with the mercury all in the vapor at 125°.5.

The specific gravity at $\frac{20^\circ}{20^\circ}$ was 0.9255; at $\frac{20^\circ}{4^\circ}$, 0.9239; at $\frac{30^\circ}{4^\circ}$, 0.9143; and at $\frac{40^\circ}{4^\circ}$, 0.9044. The coefficient of expansion calculated from the average of these determinations is 0.000918.

A chlorine determination gave the following percentage: 0.1572 gram of the oil gave 0.1872 grams AgCl.

	Calculated for $C_6H_{11}Cl$.	Found.
Cl	29.92	29.50

The molecular weight was determined at the freezing-point of benzene.

1.1641 grams of the oil and 0.1992 gram benzene gave a depression of 2°.482.

Calculated for $C_6H_{11}Cl$.	Found.
118.5	118

The index of refraction at 20° was found to be 1.416, and the molecular refraction 33.29. Required for $C_6H_{11}Cl$, 32.54. Hexamethylene is, therefore, the principal hydrocarbon with this boiling-point.

In distilling the portions of California petroleum below 100°, it has always been observed that a distillate collected at 90° to 91°. To ascertain whether a hydrocarbon were really present with this boiling-point, distillation of the fractions 85°–100° was continued through a tall Hempel column until a larger portion collected at 89° to 90°. The specific gravity of this fraction without purification was 0.7295, $\frac{20^\circ}{20^\circ}$, After thorough treatment, first with common sulphuric acid and then with fuming acid, the specific gravity was not changed (0.7295). The index of refraction of this hydrocarbon at 20° was 1.411, and the molecular refraction 33.35; calculated for C_7H_{14}, 32.22. The molecular weight at the freezing-point was found to be as follows:

0.8669 gram of the oil and 17.62 grams of benzene gave a depression of 2°.547.

Calculated for C_7H_{14}.	Found.
98	99

With the mercury column all in the vapor, bar. 745.3 mm., this hydrocarbon distilled completely at 90°.4.

The chlorine derivative of this hydrocarbon was formed by the action of chlorine over water. After washing, drying, and distillation under atmospheric pressure, the chloride came together at 145° to 150°, for the most part at 147°.

A determination of chlorine gave a value required for the monochloride:

0.1605 gram of the oil gave 0.1696 gram AgCl.

	Calculated for $C_7H_{13}Cl$.	Found.
Cl	26.77	26.13

The specific gravity of the chloride at $\frac{20°}{20°}$ was 0.9332; at $\frac{20°}{4°}$, 0.9316; at $\frac{30°}{4°}$, 0.9231; at $\frac{40°}{4°}$, 0.9138. The coefficient of expansion for 1° calculated from these results is 0.000973.

A determination of the molecular weight at the freezing-point gave the following value:

0.9318 gram of the oil and 19.98 grams of benzene gave a depression of 1°.744.

Calculated for $C_7H_{13}Cl$.	Found.
132.5	131

The index of refraction at 20° was found to be 1.441, and the molecular refraction, 37.57; calculated for $C_7H_{13}Cl$, 37.11.

These results are sufficient to establish the formula for this hydrocarbon as C_7H_{14}. It is probably dimethylpentamethylene. It differs in its properties from methylhexamethylene, boiling-point 99° to 100°: its chloride boils at 147°, while methylhexamethylene chloride boils at 141° to 142°.

Methylhexamethylene Chloride, $C_7H_{13}Cl$.

To ascertain the correct boiling-point of heptamethylene, the distillates 95°–100° were carried through a series of distillations until the greater portion collected at 98° to 100°, and this product distilled for the most part at 99° to 100°, bar. 745°.3, with the mercury column wholly in the vapor.

The empirical formula of this hydrocarbon has been ascertained in the distillates from various specimens of California oils, by analysis and determinations of molecular weight. The boiling-point of hexahydrotoluene, prepared by the addition of hydrogen to toluene, was given as 97°. Markownikoff found that the same hydrocarbon separated from Russian petroleum, and also the synthetically prepared heptanaphthene, boiled at 101°.

For further identification of our product it seemed advisable to study its derivatives. The chlorine derivative was first formed by passing chlorine into the hydrocarbon over water until the greater part was converted into the chloride. This reaction takes place very readily in ordinary daylight, and with a large generator the action of chlorine may be made continuous, saving much time in the chlorination. This method seems to be more advantageous than that formerly used by us in which dry chlorine was allowed to act on the vapor of the dry oil. The chlorinated oil was washed, dried over calcium chloride, and fractioned. After five distillations through a Hempel column, a considerable portion collected at 141° to 142°, which proved to be the monochloride, and more remained above 160°, which was doubtless the dichloride.

A determination of chlorine in the fraction 141°–142°, by the method of Carius, gave a value required for $C_7H_{13}Cl$:

0.1863 gram of the oil gave 0.2025 gram AgCl.

	Calculated for $C_7H_{13}Cl$.	Found.
Cl	26.77	26.88

The molecular weight was also determined by the Beckmann freezing-point method:

1.1960 grams of the oil and 25.8960 grams benzene gave a depression of 1°.701.

Calculated for $C_7H_{13}Cl$.	Found.
132.5	133

The specific gravity of the monochloride at 20° was found to be 0.9310. For further confirmation of the formula, the index of refraction was determined with the aid of a Pulfrich refractometer, and from the density and molecular weight the molecular refraction was calculated. The index of refraction found was 1.441, and the molecular refraction:

Calculated for $C_7H_{13}Cl$.	Found.
37.11	37.57

The theoretical value was calculated on the assumption that all the carbon atoms are singly connected.

In order to ascertain whether the chlorine atom enters the ring or side chain, the nitril was formed by heating the chloride with alcoholic potassic cyanide for several hours. There was an abundant separation of potassic chloride, and on diluting the solution the nitril separated as an oily liquid above the water. This oil had the characteristic odor of the nitrils. Its specific gravity at 20° was 0.9253, and its index of refraction 1.45. The molecular refraction, assuming the molecular weight, was 35.78, calculated from the elements, assigning to the cyanogen group the value 5.33, which was determined from ethyl cyanide, C_2H_5CN. The theoretical molecular refraction for the nitril calculated on the same basis is 36.45.

The nitril was saponified by heating it to 110° with concentrated hydrochloric acid. The acid formed had the odor of alphatoluic acid, but the amount obtained was not sufficient for complete examination.

When heptamethylene chloride was brought together with metallic sodium, a vigorous action soon set in with the evolution of great heat, sufficient to cause the decomposition of the products unless it was controlled by cooling. This reaction was best carried on by dissolving the chloride in ether, adding the sodium in slight excess over the calculated amount, and keeping the solution cold. In two hours the reaction was complete. The products included an unsaturated hydrocarbon, boiling-point 97°, and another hydrocarbon, boiling-point approximately 220° to 230°. That the hydrocarbon boiling at 97° was unsaturated was shown by the formation of a bromine addition-product; bromine was added readily in the cold with no escape of hydrobromic acid. A Carius determination of the bromine in this product gave the following result:

0.2045 gram of the oil gave 0.3023 gram AgBr.

	Calculated for $C_7H_{12}Br_2$.	Found.
Br	62.5	62.9

The specific gravity of the dibrom derivative at 20° was 1.648. A determination of its molecular weight was made:

0.9238 gram of the oil and 25.3 grams of benzene gave a depression of 0°.725.

Calculated for $C_7H_{12}Br_2$.	Found.
256	247

The odor of the unsaturated hydrocarbon was very sharp and penetrating, very different from that of the paraffin and methylene hydrocarbon, but resembling the olefines. In further proof that it contained doubly bonded carbon, it was titrated with the Hübl reagent, an alcoholic solution of iodine and mercuric chloride. The amount of iodine absorbed was approximately equivalent to two atoms of iodine for each molecule of the hydrocarbon. When heated with hydriodic acid, the monoiodide was readily formed. The specific gravity of the unsaturated hydrocarbon at 20° was 0.7472. Its molecular weight was ascertained by the freezing-point method:

0.7116 gram of the oil and 25.19 grams of benzene gave a depression of 1°.420.

Calculated for C_7H_{12}.	Found.
96	98

The index of refraction of sodium light was found to be 1.416. The molecular refraction calculated from the density and molecular weight was:

Calculated for		
$C_6H_9CH_3$.	$C_6H_{10}{=}CH_2$.	Found.
30.06	31.77	32.34

These values indicate that the unsaturated hydrocarbon contains a double bond between the side-chain carbon and a carbon atom in the ring, confirming the position of the chlorine atom in the side chain, which is indicated by the ease with which it is replaced in the reaction with potassic cyanide. The form that the chlorination takes doubtless depends on the fact that the hydrogen in the side chain is less firmly bound than the hydrogen atoms in the methylene ring. The unsaturated condition $C_6H_{10}=CH_2$ is shown by the action of halogens and haloid acids, and confirmed by the molecular refraction, which corresponds to the sum of the atomic refractions assuming the double bond.

This constituent of California petroleum is therefore identical with methylhexamethylene, which may be formed by the addition of hydrogen to toluene.

The hydrocarbon with a boiling-point 220° to 230°, formed by the action of sodium on methylhexamethylene chloride, doubtless contains two methylene rings :

$$C_6H_{11}CH_2—CH_2C_6H_{11}.$$

The quantity of this product formed was too small for identification, but it evidently affords a means for building up the higher methylene hydrocarbons containing more than one methylene ring. That it was a condensed hydrocarbon was shown by its high specific gravity, 0.8872.

Dimethylhexamethylene Chloride, $C_8H_{15}Cl$.

The formula of dimethylhexamethylene was ascertained, as shown in the previous paper, by analysis and determination of its molecular weight. The formula was still further verified by the formation of the chlorine derivative. As in the chlorination of methylhexamethylene, chlorine was allowed to act on the hydrocarbon over water in ordinary daylight until it was nearly all converted into the chlorine derivative. After washing and drying, the product was distilled under atmospheric pressure; after several distillations the monochloride collected in larger part at 168° to 170°. The specific gravity of this product at 20° was found to be 0.9358. A determination of chlorine gave the following result :

0.2034 gram of the oil gave 0.1973 gram AgCl.

	Calculated for $C_8H_{15}Cl$.	Found.
Cl	24.21	24.01

The molecular weight of the chloride was determined by the freezing-point method :

0.7293 gram of the oil and 25.66 grams benzene gave a depression of 0°.982.

Calculated for $C_8H_{15}Cl$.	Found.
146.5	142

The index of refraction for sodium light at 20° was 1.455, and the molecular refraction:

Calculated for $C_8H_{15}Cl$.	Found.
41.69	41.60

That the chlorine enters a side chain in this reaction, as in the case of methylhexamethylene, appears from the ready formation of the nitril by heating the chloride with alcoholic potassic cyanide. On diluting the solution the nitril separated as an oil, with the characteristic odor of the nitrils. It was saponified by heating with aqueous potassic hydrate. On acidifying the solution, a solid was precipitated with an odor characteristic of the α-toluic acids, but the quantity obtained was not sufficient for identification. It was probably metamethyl-α-toluic acid.

Trimethylhexamethylene Chloride, $C_9H_{17}Cl$.

This chloride was also formed, washed, dried, and fractioned under atmospheric pressure. It came together in larger quantity at 186°–188°; its specific gravity at 20° was 0.9380. The percentage of chlorine was determined.

0.2300 gram of the oil gave 0.2041 gram AgCl.

	Calculated for $C_9H_{17}Cl$.	Found.
Cl	22.10	21.94

The molecular weight was also ascertained at the freezing-point:

0.8672 gram of the oil and 25.03 grams benzene gave a depression of 1°.090.

Calculated for $C_9H_{17}Cl$.	Found.
160.5	156

In further support of the formula of the chloride, the index of refraction was determined, 1.462, and the molecular refraction calculated.

Calculated for $C_9H_{17}Cl$.	Found.
46.3	47

When sodium was allowed to act on trimethylhexamethylene chloride, a vigorous reaction set in that could be controlled by cooling. By carrying on the reaction in an ethereal solution on standing over night in water the reaction was complete. The product of the reaction consisted for the most part of an unsaturated hydrocarbon, and a smaller quantity of a heavy oil, doubtless formed by the union of two methylene rings. The boiling-point of the unsaturated hydrocarbon was 135° to 140°. Its unsaturated condition was shown by the readiness with which it united with iodine in Hübl's reagent, absorbing approximately 2 atoms of iodine. The specific gravity of the unsaturated hydrocarbon at 20° was 0.7762. The molecular weight at the freezing-point was determined.

0.8572 gram of the oil and 22.45 grams benzene gave a depression of 1°.571.

Calculated for C_9H_{16}.	Found.
124	120

The index of refraction was found to be 1.431, and the molecular refraction:

Calculated for $C_6H_7(CH_3)_3$.	Calculated for $C_6H_8(CH_3)_2=CH_2$.	Found.
39.26	40.97	41.46

Dekanaphthene Chloride, $C_{10}H_{19}Cl$.

In confirmation of the formula of dekanaphthene, the index of refraction was determined and the molecular refraction calculated. The density 0.7898, the index 1.4325, and the molecular weight gave the following value:

Calculated for $C_{10}H_{20}$.	Found.
46.10	46.00

The chlorine derivative of this hydrocarbon was formed by passing in chlorine over water. After washing, drying, and fractioning *in vacuo*, the chloride collected in larger quantities at 105° to 110° (50 mm.). Another portion collected at 140° to 145°, probably a dichloride. The specific gravity of the monochloride at 20° was 0.9470. A determination of chlorine gave the following value:

0.1840 gram of the oil gave 0.1476 gram AgCl.

	Calculated for $C_{10}H_{19}Cl$.	Found.
Cl	20.33	19.80

The molecular weight of the chloride at the freezing-point of benzene was also determined:

1.2536 grams of the oil and 21.29 grams benzene gave a depression of 1°.689.

Calculated for $C_{10}H_{19}Cl$.	Found.
174.5	171

A determination of the index of refraction of this chloride gave 1.468. The molecular refraction was calculated as follows:

Calculated for $C_{10}H_{19}Cl$.	Found.
50.89	51.34

On account of the small quantity of the dichloride obtained, it was not possible to purify it completely by distillation. But a determination of chlorine gave 31.53 per cent; required for $C_{10}H_{18}Cl_2$, 33.90. A determination of molecular weight gave 199; required for the dichloride, 209. The molecular refraction calculated from the index was 56.98; calculated from the formula, 55.81. On account of the differences between the theoretical values for the mono- and dichlorides, these values are sufficient to show that the dichloride was formed and separated in nearly a pure form.

Undekanaphthene Chloride, $C_{11}H_{21}Cl$.

The index of refraction of this hydrocarbon was found to be 1.4403, and the molecular refraction:

Calculated for $C_{11}H_{22}$.	Found.
50.70	50.63

This determination was made in the distillate 190°–192°, which was used for all work on this hydrocarbon.

The chlorine derivative was prepared in the same manner as those of the hydrocarbons previously described. On fractioning it *in vacuo* at 35 mm. it collected for the most part at 125° to 130°. Its specific gravity was found to be 0.9583 at 20°. A chlorine determination supported the formula of the monochloride.

0.1560 gram of the oil gave 0.1179 gram AgCl.

Calculated for $C_{11}H_{21}Cl$.	Found.
18.81	18.69

The molecular weight was determined at the freezing-point of benzene.

0.6055 gram of the oil and 17.37 grams benzene gave a depression of 0°.890.

Calculated for $C_{11}H_{21}Cl$.	Found.
188.5	192

The index of refraction was found to be 1.476, and the molecular refraction:

Calculated for $C_{11}H_{21}Cl$.	Found.
55.48	54.32

The composition of its chloride, together with its molecular weight and molecular refraction, all show that the boiling-point of undecane is 194° to 196°.

Dodekanaphthene Chloride, $C_{12}H_{23}Cl$.

The index of refraction of dodekanaphthene was found to be 1.4649, and the molecular refraction:

Calculated for $C_{12}H_{24}$.	Found.
55.38	55.24

The chlorine derivative was formed, washed, dried, and fractioned *in vacuo*. It collected for the most part at 130°–135° (17 mm.). Its specific gravity at 20° was 0.9616. A determination of chlorine gave the following result:

0.1657 gram of the oil gave 0.1153 gram AgCl.

	Calculated for $C_{12}H_{23}Cl$.	Found.
Cl	17.52	17.20

The molecular weight was also determined:

0.7172 gram of the oil and 19.04 grams benzene gave a depression of 0°.925.

Calculated for $C_{12}H_{23}Cl$.	Found.
202.5	204

The index of refraction was 1.480, and the molecular refraction:

Calculated for $C_{12}H_{23}Cl$.	Found.
60.77	59.96

Tridekanaphthene Chloride, $C_{13}H_{25}Cl$.

The index of refraction of this hydrocarbon as determined is 1.4745, and its molecular refraction:

Calculated for $C_{13}H_{26}$.	Found.
60.25	59.84

The chlorine derivative was formed by the action of chlorine, dried and fractioned under 17 mm.; it came together for the most part at 140° to 145°. Its specific gravity at 20° was 0.9747; a Carius determination gave the following percentage of chlorine:

0.1674 gram of the oil gave 0.1137 gram AgCl.

Calculated for $C_{13}H_{25}Cl$.	Found.
16.38	16.78

In the chlorine derivatives of the higher hydrocarbons the weight of the oil that can be taken for analysis is limited, since as in the last analysis the pressure of the large volume of gases formed is more than the tube can stand. The molecular weight of tridekanaphthene chloride was determined at the freezing-point of benzene:

0.4447 gram of the oil and 17.88 grams benzene gave a depression of 0°.763.

Calculated for $C_{13}H_{25}Cl$.	Found.
216.5	217

Tetradekanaphthene Chloride, $C_{14}H_{27}Cl$.

Tetradekanaphthene chloride was readily formed by passing chlorine into the hydrocarbon over water in ordinary daylight; if the action was stopped with a small portion of the hydrocarbon unacted on, the product consisted for the larger part of the monochloride. After washing and drying, the chlorine derivative was separated by continued distillation *in* *vacuo* under 13 mm.; it came together for the most part at 150° to 155°. The specific gravity of the monochloride was 0.9748, $\frac{20^\circ}{20^\circ}$; at $\frac{20^\circ}{4^\circ}$, 0.9730; at $\frac{30^\circ}{4^\circ}$, 0.9661; and at $\frac{40^\circ}{4^\circ}$, 0.9579. The mean coefficient of expansion, within 20° to 40°, from these results, is 0.00078.

A determination of chlorine gave a value required for the monochloride:

0.1559 gram of the oil gave 0.0989 gram AgCl.

	Calculated for $C_{14}H_{27}Cl$.	Found.
Cl	15.39	15.80

As mentioned above, the decreasing proportion of chlorine in these derivatives with the increasing molecular weight, and the consequent larger volumes of gases, beyond the strength of the ordinary Carius tubes, gives a smaller weight of silver chloride than could be desired, but the accuracy of the method permits of sufficiently reliable results, even with the small weights.

The molecular weight of the chloride was determined at the freezing-point of benzene:

0.8923 gram of the oil and 17.76 grams benzene gave a depression of 1°.094.

Calculated for $C_{14}H_{27}Cl$.	Found.
230.5	225

The index of refraction was found to be 1.493, and the molecular reaction 68.67; calculated for $C_{14}H_{27}Cl$, 69.37.

The boiling-point of this chloride cannot be accurately determined under atmospheric pressure because it is rapidly decomposed at the higher temperature and in presence of air, although it may be distilled indefinitely *in vacuo*. Probably the boiling-point under atmospheric pressure is not far from 275°.

Pentadekanaphthene Chloride, $C_{15}H_{29}Cl$.

This chloride was prepared from pentadekanaphthene which had been well fractioned *in vacuo*. These higher chlorides are formed as readily as the lower ones. After washing and fractional distillation under 14 mm. this monochloride came together for the most part at 170° to 175° without decomposition. Its boiling-point under atmospheric pressure is probably near 300°. Its specific gravity at $\frac{20^\circ}{20^\circ}$ was 0.9771; at $\frac{20^\circ}{4^\circ}$, 0.9753; at $\frac{30^\circ}{4^\circ}$, 0.9714; and at $\frac{40^\circ}{4^\circ}$, 0.9643. The coefficient of expansion calculated from these values is 0.000576. A Carius determination gave the required percentage of chlorine.

0.1536 gram of the oil gave 0.0923 gram silver chloride.

Calculated for $C_{15}H_{29}Cl$.	Found.
14.51	14.85

A determination of the molecular weight supported the same formula.

0.9073 gram of the oil and 18.93 grams benzene gave a depression of 0°.984.

Calculated for $C_{15}H_{29}Cl$.	Found.
244.5	239

The index of refraction was 1.493, and the molecular refraction 72.90; calculated for $C_{15}H_{29}Cl$, 73.97.

Attempts will be made to form the chlorides of the higher hydrocarbons in connection with the study of the composition of these bodies.

XXXVII.—ON THE COMPOSITION OF JAPANESE PETROLEUM.

BY CHARLES F. MABERY AND SHINICHI TAKANO.[1]

The oil fields in Japan are the most promising and are under the most rapid development of any recently discovered oil territory. The output in 1891 was 56,000 bbls. annually; in 1899 it was 1,000,000 bbls. The oil territory in Japan is contained in the province of Echigo, at least to the extent of 90 per cent on the northern coast of the Sea of Japan. This province is surrounded in part by a mountain chain which encloses a section of country 140 miles long by 150 miles broad, rising gradually from the sea to the mountains with a varying altitude from 150 to 500 feet. Oil is found chiefly in the Upper Eocene of the Tertiary formation, where it is held under pressure between impervious layers of slate and sandstone.

---

[1] Mr. Takano has spent three years in the study of petroleum in this country, having been sent for this purpose by the Japanese government. He is thoroughly familiar with the geology of the oil territory in Japan, having given especial attention to this subject in a thesis which he presented for a degree in the University of Tokio. Besides a thorough knowledge of the composition of petroleum from a chemical point of view, which he has gained during the two years he has spent exclusively in the study of this subject in this laboratory, Mr. Takano spent one year as a laborer in different refineries, where he took charge by actual manipulation of every process in the preparation of commercial products. The work presented in this paper formed the subject of a thesis by Mr. Takano for the degree of M.S.

Nodules of calcite are frequently found embedded in the sandstone, and crystals of calcite twinned, resembling those found in the Ohio Trenton-limestone, oil-bearing rock. The oil strata are full of sea shells, a good indication as to the origin of the oil formations. There are great variations in the depths of the wells. For example, the wells of the Amaze field are approximately 2,000 feet in depth, while those of the Miyagawa field, only 6 miles distant, are 700 feet deep. The wells of the Niitsu field are still shallower, 600 feet. The Nagaoka wells are 800 feet in depth. Nevertheless, the oil strata at the different depths are essentially of the same formation. The sandstone in which the Nagaoka oil is found is coarser than that of the other fields. On the surface of the Niitsu oil territory are immense beds of peat which are used for fuel.

Although the oil fields of Japan are situated in close proximity, specimens of oil from the different fields differ as essentially in composition as the variations in specific gravity indicate. As will appear later, the Amaze, Miyagawa, and Hirei fields yield paraffin in considerable quantities. While the hydrocarbons above C_7H_{14} do not include members of the series C_nH_{2n+2}, at least so far as it appears from analysis of distillates prepared on a laboratory scale, the lower distillates do contain members of the paraffin series.

The paraffin hydrocarbons with low boiling-points, such as the butanes, pentanes, and hexanes, have an agreeable sweetish odor that is easily recognizable, and quite different from the pungent harsh odor of the methylenes. The odor of the paraffins is more apparent in the Miyagawa oil than in any other of the Japanese oils we have seen, and somewhat less in the Amaze oil. When these hydrocarbons with low boiling-points are present, the crystalline paraffin hydrocarbons C_nH_{2n+2} are usually to be found.

Considerable quantities of gas were formerly obtained from the Amaze oil territory, but the supply now seems to be exhausted, at least so far as wells have been bored; some gas escapes from the shallow Miyagawa wells, more from the shallow wells of the Niitsu territory. As wells are sunk deeper in this territory it is probable that lighter oils will be found. On account of the friable condition of the oil rock and the danger of clogging the wells by loose material, "shooting" the wells after boring is not practiced. The flow from the wells is irregular; frequently it will amount to 300 barrels a day for a week, and then stop, and the oil must be pumped.

The oil territory in Japan includes the following fields: Amaze, Nagaoka, Niitsu, and Hiyama. The different sections of the oil territory may be classified as follows:

Amaze	Amaze Miyagawa Gendogi	green oil
Nagaoka	Hirei Kitatani Katsudo	dark oil
Niitsu	Koguchi Kusodsu	
Hiyama	Hiyama	dark green oil.

The Amaze field is the oldest; the Hiyama field has been most recently developed; both these oils contain paraffin.

The crude oils from the different fields differ essentially in their properties, as shown by the different specific gravity, the different percentages of sulphur, nitrogen, and the differ-

	Amaze.	Hirei.	Katsudo.	Kitatani.
Specific gravity	0.8245	0.8622	0.8771	0.8952
Per cent sulphur	0.23	0.41	0.82	0.61
" nitrogen	0.35	0.74	0.97	0.75
Iodine absorption	0.0	0.84	7.66	0.82
Coefficient of expansion	82.5	78.5	76.5	79.5

	Koguchi.	Kusodsu.	Miyagawa.
Specific gravity	0.9435	0.9210	0.8911
Per cent sulphur	0.49	0.37	0.32
" nitrogen	1.34	1.23	0.55
Iodine absorption	9.79	0.62	1.63
Coefficient of expansion	67.5	61.5	74.5

Percentages of Distillates.

	Amaze.	Hirei.	Katsudo.	Kitatani.	Koguchi.	Kusodsu.	Miyagawa.
−150°	22.8	21.8	22.2	14.0	0.0	0.0	15.0
150°–300°	40.2	38.3	38.8	38.8	25.0	25.0	36.8
+300°	37.0	39.9	39.0	47.2	75.0	75.0	48.2

ent proportions in which they distil at different temperatures. There are also marked differences in iodine absorption, and in the coefficients of expansion. The latter were determined by ascertaining the specific gravity at 5°, 10°, 20°, and 25°, and dividing the differences in specific gravity at the different temperatures by 5 and multiplying the quotient by 100,000, the method described in Redwood's treatise on petroleum.

In the development of oil territory hitherto, no attempts have been made to ascertain the series of hydrocarbons which compose the main body of the crude oil. Beside the work of Pelouze and Cahours, Schorlemmer, and Warren on the Pennsylvania and Canadian oils, and the work carried on in this laboratory, no attempts have been made to determine the form of the hydrocarbons in the lower distillates of American oils, and nothing whatever beside the unpublished work of this laboratory on the determination of the composition of the portions with higher boiling-points. Beside the work of Markownikoff on the Russian oils and the work of Warren and Storer on Rangoon petroleum, very little has been done in this direction on oils from other fields. On account of the ease in the preparation of commercial products from the lighter oils of Pennsylvania and Ohio, the ultimate composition was of less importance than it is now becoming in the development of oil fields that yield heavier crude oils, such as the oil territory in California, Texas, South America, Japan, and numerous other fields recently discovered. The methods that must be applied to these heavy oils are essentially different from the methods that have been universally in use since the beginning of the oil industry. In Japan, the promoters of those oil fields will have the advantage not only of all former experience in oil refining, but the further advantage of a knowledge of the hydrocarbons which form the main body of the crude oils. Japanese petroleum apparently differs from other heavy petroleums in that it contains smaller amounts of the homologues of benzene. Benzene and its homologues were found in the Amaze oil, and some of the other crude oils, but fuming sulphuric acid failed to reduce materially the specific gravity of several of the distillates that should yield benzene hydrocarbons, if they were present.

Constituents of Petroleum from the Amaze Field.

The lightest oil from the Japanese fields is found in the Amaze territory. It consequently contains the largest proportion of more volatile constituents. A combustion of Amaze crude oil gave 84.66 per cent carbon and 13.22 per cent hydrogen. After several distillations under a Hempel column, fractions collected in larger quantities at 68°, 98°, 119°, 135°, 162°, 196°, 216°. No attempts were made to ascertain the form of the hydrocarbons below 68°. The distillate collected at 68° had the specific gravity 0.7343, which indicated that hexane was not present in any considerable quantity; but nothing further was done toward identifying hexamethylene, which no doubt is the principal hydrocarbon in this distillate.

The distillate collected at 98° to 100°, after purifying with fuming sulphuric acid, gave as its specific gravity, at 20°, 0.7450.

A combustion gave the following percentages of carbon and hydrogen:

0.1347 gram of the oil gave 0.4221 gram CO_2 and 0.1721 gram H_2O.

	Calculated for C_7H_{12}.	Found.
C	85.70	85.45
H	14.30	14.20

Its index of refraction was found to be 1.4174, and the molecular refraction, 33.14; calculated for C_7H_{14}, 32.22. This hydrocarbon was therefore methylhexamethylene.

The distillate 118°–120°, after purification with fuming sulphuric acid, gave 0.7621 as its specific gravity at 20°. A combustion gave the following percentages of carbon and hydrogen:

0.1406 gram of the oil gave 0.4378 gram CO_2 and 0.1812 gram H_2O.

	Calculated for C_8H_{16}.	Found.
C	84.70	84.94
H	14.30	14.33

A determination of the index of refraction of this oil gave 1.4256, and the molecular refraction 37.68; calculated for C_8H_{16}, 36.82. This hydrocarbon was therefore dimethylhexamethylene.

The distillate collected at 134° to 135°, was purified with fuming sulphuric acid and analyzed.

0.1528 gram of the oil gave 0.4805 gram CO_2; and 0.1950 gram H_2O.

	Calculated for C_9H_{18}.	Found.
C	85.70	85.76
H	14.30	14.29

Its specific gravity, at 20°, was 0.7787.

The refractive index of this oil was found to be 1.4348, and the molecular refraction 42.27; calculated for C_9H_{18}, 41.42. This constituent was therefore trimethylhexamethylene.

A distillate collected in considerable quantity at 160° to 162°, which was purified with fuming sulphuric acid and analyzed:

0.2055 gram of the oil gave 0.6445 gram CO_2; and 0.2556 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.50
H	14.30	13.82

This oil had the specific gravity, 0.7902, at 20°. Its index of refraction was 1.4418, and its molecular refraction 46.94; calculated for $C_{10}H_{20}$, 46.03.

The distillate at 190° to 192°, after purification with fuming sulphuric acid, had the specific gravity, 0.8061, at 20°. Its composition was determined by analysis:

0.1612 gram of the oil gave 0.5046 gram CO_2; and 0.2025 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	85.35
H	14.30	13.96

The molecular weight of this hydrocarbon at the freezing-point of benzene was 166; calculated for $C_{11}H_{22}$, 154. The index of refraction at 20° was 1.4482, and the molecular refraction 51.24; calculated for $C_{11}H_{22}$, 50.63.

The distillate 212°–214°, purified with fuming sulphuric acid, had the specific gravity, 0.8165, at 20°. A combustion gave the following proportions of carbon and hydrogen:

0.1875 gram of the oil gave 0.5879 gram CO_2 and 0.2451 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	85.70	85.51
H	14.30	14.52

A determination of its molecular weight at the freezing-point gave 172; calculated for $C_{12}H_{24}$, 168. Its index of refraction was 1.4535, and the molecular refraction 55.76; calculated for $C_{12}H_{24}$, 55.23.

Composition of the Portions of Japanese Petroleum with High Boiling-points.

Japanese petroleum from different sources differs materially in its composition. From such oils as the Hirei no crystalline solids can be separated even at low temperatures. But from others, such as the Amaze, Miyagawa, and Hiyama, crystalline solids separate from the higher fractions. The fraction 310°–315° atmospheric pressure, from Amaze crude oil became solid on cooling. The solid portion was separated by cooling and filtration; it was washed, pressed, and warmed with gasoline, which removed all color. Melting-point, 68°. The fractions between 225° were collected *in vacuo* under 30 mm. The purified solid from 225° to 230° melted at 70°, that from 250° to 275° at 73°, and that from 260° to 265° at 74°. The solid from 225° to 230° gave, by combustion, values showing it to belong to the series C_nH_{2n+2}.

0.1535 gram of the oil gave 0.4890 gram CO_2 and 0.1787 gram H_2O.

	Calculated for		Found.
	$C_{12}H_{24}$.	C_nH_{2n}.	
C	85.14	85.70	85.29
H	14.86	14.30	14.99

The fraction 250°–260°, 30 mm., from the Amaze oil, gave the following percentages by combustion, also showing the series C_nH_{2n+2} :

0.1654 gram of the oil gave 0.5161 gram CO_2; and 0.2233 gram H_2O.

C	85.03
H	15.00

A combustion of the fraction 265°–270° gave values required for a hydrocarbon of the series C_nH_{2n+2} :

0.1750 gram of the oil gave 0.5469 gram CO_2; and 0.2346 gram H_2O.

C	85.21
H	14.81

In determining the molecular weight of this hydrocarbon at the boiling-point of benzene, the following result was obtained :

0.4190 gram of the oil and 24.3 grams benzene gave a rise in boiling-point of 0.126.

Calculated for $C_{26}H_{54}$.	Found.
367	367

Determinations by the boiling-point method of hydrocarbons with such high molecular weights are of necessity somewhat uncertain on account of the slight rise in boiling-point. The question of the molecular weights of these solid hydrocarbons will receive more attention with the constituents of Pennsylvania and California petroleums with high boiling-points.

The specific gravity of the solid 250°–260° is nearly the same as that of the corresponding hydrocarbon from Pennsylvania petroleum :

	Japanese. 250°–260°, 30 mm.	Pennsylvania,[1] 292°–295°, 50 mm.
60		0.7977
70	0.7943	0.7950
80	0.7920	0.7943
90	0.7918	

[1] Unpublished data.

The specific gravity of the Japanese solid at 60° could not be determined, because it was not liquid at that temperature.

Miyagawa Petroleum.

Although this oil is from a field situated only six miles from the Amaze field, it differs essentially in its specific gravity, and in the proportions in which it distils, from the Amaze oil. The crude oil was distilled under atmospheric pressure, and the distillation of the lower portions continued until they came together in larger quantities at temperatures at which distillates were collected from the other oils. The specific gravity of the distillates, after treating with concentrated sulphuric acid, is as follows:

98°–100°.	118°–120°.	134°–136°.	160°–162°.	194°–196°.	212°–214°.	228°–130°.
0.7364	0.7631	0.7772	0.8088	0.8493	0.8674	0.8770

The last three fractions were also treated with fuming sulphuric acid and the specific gravity determined;

194°–196°.	212°–214°.	228°–230°.
0.8412	0.8650	0.8720

The slight change after the thorough treatment with fuming sulphuric acid shows that no homologues of benzene were present in these portions, yet the specific gravity of the hydrocarbons above 196° is considerably higher than of those from Amaze oil or from Hirei oil. The distillates collected under atmospheric pressure were thoroughly treated with fuming sulphuric acid, washed, dried, and their molecular refraction determined:

Distillate.	Refractive index.	Molecular refraction. Calculated.	Molecular refraction. Required.
98°–100°	1.4117	33.14	32.21
118°–120°	1.4163	36.92	36.82
134°–136°	1.4261	41.51	41.42
160°–162°	1.4463	46.26	46.03
194°–196°	1.4605	50.27	50.63
214°–216°	1.4706	54.34	55.23

Hirei Petroleum.

A combustion of Hirei crude oil gave 82.28 per cent of carbon and 13.19 per cent of hydrogen. In the distillation of the Hirei oil, fractions collected within the same limits of temperature as those from the other crude oils. The distillate collecting in the vicinity of 98°, after treatment with sulphuric acid, gave 0.7412 as its specific gravity. Its molecular weight at the freezing-point of benzene was 98; required for C_7H_{14}, 98. Its index of refraction was 1.4095, and its molecular refraction, 32.77; required for C_7H_{14}, 32.22.

The fraction 118°–120° had the specific gravity 0.7523. Its molecular weight was 114; required for C_8H_{16}, 112. Its index of refraction was 1.4151, and its molecular refraction 37.34; required for C_8H_{16}, 36.82.

The fraction at 135° had the specific gravity 0.7676. Its molecular weight was 128; required for C_9H_{18}, 126. Its index of refraction was 1.4372, and its molecular refraction 42.12; required for C_9H_{18}, 41.42.

The fraction 162° had the specific gravity 0.7887. Its molecular weight was found to be 137; required for $C_{10}H_{20}$, 140. Its index of refraction was 1.4372, and its molecular refraction 46.60; required for $C_{10}H_{20}$, 46.03.

The specific gravity of the fraction at 196° was 0.8192. Its index of refraction was 1.4516, and its molecular refraction 50.78; required for $C_{11}H_{22}$, 50.63.

The specific gravity of the fraction 216° was 0.8327, and the molecular weight 172; required for $C_{12}H_{24}$, 168. Its index of refraction was 1.4599, and its molecular refraction, 55.22; required for $C_{12}H_{24}$, 55.23.

The specific gravity of these distillates from Hirei oil is somewhat higher than was found in the corresponding distillates from Amaze oil, and the differences increase with increasing molecular weights. It was at first thought that this was due to incomplete removal of benzene hydrocarbons, but still further treatment with fuming sulphuric acid failed to diminish these values. It is probable that the oil contains hydrocarbons with more than one methylene ring.

The results of this examination show that Japanese petroleum is composed for the greater part of hydrocarbons of the series C_nH_{2n},—the methylene hydrocarbons. Probably the very heavy oils contain hydrocarbons with two or more methylene rings, of the series C_nH_{2n-2} or C_nH_{2n-4}. Some of the oils contain solid paraffin hydrocarbons, others do not.

The proportion of benzene derivatives in the oils examined is relatively much smaller than in California petroleum. The proportion of nitrogen compounds and of sulphur compounds is quite variable. In some of the oils the percentages were nearly as large as any found in California petroleum, in others the amounts were much smaller.

THE BASIC NITRATES OF BISMUTH.

BY F. B. ALLAN.

When bismuth nitrate is treated with water, it is decomposed, forming a basic nitrate, $BiONO_3$, which has been described by Duflos,[1] Heintz,[2] Becker,[3] Ditte,[4] and others. It is said to have one, two, or three molecules of water of crystallization, according to the method of preparation.

Numerous other basic nitrates have also been described:

A. $6Bi_2O_3.5N_2O_5 + 9H_2O$.—Bismuth nitrate, or a solution of bismuth in nitric acid, is added to water above 50° (Becker).

B. $5Bi_2O_2.4N_2O_5 + 9H_2O$.—A solution of bismuth nitrate is added to water at 40° to 50°; after twenty-four hours three-quarters of the liquid is poured off and more water at 50° is added; when the liquid has cleared, the precipitate is filtered off and washed with cold water (Becker).

C. $11Bi_2O_3.9N_2O_5 + 21H_2O$.—Same preparation as *B* (Janssen).[5]

D. $4Bi_2O_3.3N_2O_5 + 9H_2O$.—*A* is washed till the wash-water gives no acid reaction (Becker).

E. $5Bi_2O_3.3N_2O_5 + 8H_2O$.—(*a*) The salt $BiONO_3$ is dissolved in a large quantity of water which, after some time, deposits a precipitate without crystalline structure (Becker).

(*b*) The salt $BiONO_3$ is mixed with twenty-four times its weight of water and dilute sodium hydroxide is added till the liquid scarcely reddens litmus (Duflos, Janssen).

F. $2Bi_2O_3.N_2O_5 + H_2O$.—The salt $BiONO_3$ is decomposed by water at 100° (Ditte).

---

[1] Archiv. der Pharm., [2], **23**, 307; Pharm. Centrbl., 1840.

[2] J. prakt. Chem., **45**, 102.

[3] Archiv. der. Pharm., **55**, 31, 129; Ann. Chem. (Liebig), **68**, 282.

[4] Compt. rend., **79**, 956.

[5] Archiv. der Pharm., **68**, 1, 129; Forts. der Chem., 1851.

It will be seen that, in most of the above preparations, no account of the composition of the mother-liquor is given. Ditte has shown that water at 10° will decompose the neutral nitrate, giving the so-called subnitrate ($BiONO_3$), only until it contains 83 grams of nitric anhydride per liter, and that a nitric acid solution stronger than that does not decompose bismuth nitrate. He also found that, at 100°, the change from the form $BiONO_3$ to the form $2Bi_2O_3.N_2O_5$ took place only when the water contained less than 4.5 of grams of nitric anhydride per liter, and that this reaction was reversible, the subnitrate being again formed when more acid was added to the solution.

The directions for preparing some of these basic nitrates were followed, and Table *A* contains a comparison of the products with those analyzed by Becker and Janssen. The bismuth was estimated as oxide by ignition of the basic nitrate, or, if in solution, by boiling with an excess of a solution of sodium carbonate and ignition of the precipitate, or by evaporation of the solution to dryness and ignition of the residue. The nitric acid was determined by boiling for half an hour with an excess of a solution of sodium carbonate, and estimation of the excess after filtering.

Table A.

			Becker.		Janssen.	
	Bi_2O_3.	N_2O_5.	Bi_2O_3.	N_2O_5.	Bi_2O_3.	N_2O_5.
A	79.65	16.81	79.86	15.55		
B,*C*	78.95	15.93	79.6	14.6	80.17	14.0
D	80.16	15.11	79.2	13.8		
E(*b*)	83.14	12.71	84.3	11.8		

This indicates that the composition of the different products is dependent on conditions which have not been described, and that possibly an examination of these conditions would show that some of these basic nitrates are mixtures. Janssen has endeavored to represent them all as consisting of

$$Bi(NO_3)_3 + 5H_2O \text{ and } 5Bi_2O_3.3N_2O_5 + 8H_2O$$

in varying proportions.

Prof. Miller suggested to me the application of the "phase rule" to this problem. In a system containing bismuth oxide, nitric anhydride, and water, five phases would constitute a nonvariant system, and a liquid, a gas, and three solid phases could exist only at one temperature, one pressure, and one concentration of the liquid for any three given solid phases. If the system consisted of a liquid, a gas, and two solid phases, it would be monovariant, and we might have such a system at different temperatures or with different concentrations of the liquid, but, at any given temperature, the liquid in equilibrium with two given solid phases could not vary in concentration. In a divariant system, one solid phase might be in equilibrium, at constant temperature, with a liquid of varying concentration, or with a liquid of given concentration at different temperatures. A knowledge of the conditions of equilibrium in such a system will enable us to determine whether one or two solid phases are present.

Neutral bismuth nitrate, or a basic nitrate of known composition, was added to water or a solution of nitric acid, and stirred in a water-bath, at constant temperature, till equilibrium was reached. It was found that these reacted more quickly than bismuth oxide and nitric acid. The stirrer was driven by a water motor and had bottles on both sides of a horizontal shaft in such a way that the contents were thrown from one end of the bottle to the other. The acidity of the liquid was determined from time to time, and when this had become constant the bismuth oxide in solution was also determined, and the difference between the bismuth oxide and nitric anhydride used, and the amount of these in solution gave the composition of the solid contents of the bottles.

The bismuth nitrate used was Kahlbaum's preparation, and the basic nitrate used in the first series of experiments was prepared from it by adding the solution in nitric acid to a large volume of cold water and filtering off the precipitate as soon as it had settled to the bottom of the vessel. There seems to be no difficulty about the preparation of this substance, as repeated experiments gave the same product. One specimen which had been dried in the air for a week gave the following results on analysis :

	Calculated for $BiONO_3 + H_2O$.	Found.
Bi	68.37	68.25
NO_3	20.35	20.30

Table B.

Temp., 21°. $\frac{Bi_2O_3}{N_2O_5}$ in $BiONO_3 = 4.31$; in $6Bi_2O_3.5N_2O_5 = 5.17$.

No.	Salt used.	Components used.			Acidity of liquid.		Bi_2O_3 in solution. Grams.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
		Bi_2O_3. Grams.	N_2O_5. Grams.	H_2O. cc.	6 days. N.	13 days. N.		
1	$BiONO_3$	1.52	0.351	40	0.0293	0.0293	....	5.24
2	“	3.04	0.703	40	0.054	0.054	....	5.15
3	“	4.56	1.054	40	0.085	0.085	....	5.22
4	“	7.59	1.757	40	0.144	0.145	....	5.25
5	“	1.52	0.673	40		0.184	0.08	5.16
6	“	3.04	1.025	40		0.212	0.10	5.15
7	“	4.55	1.376	40		0.244	0.14	5.17
8	“	6.07	1.727	40	0.267	0.277	0.16	5.21
9	“	1.52	0.866	40		0.283	0.17	5.13
10	“	3.04	1.217	40		0.318	0.21	5.25
11	“	4.56	1.568	40	0.312	0.349	0.28	5.09
12	“	6.07	1.92	40	0.328	0.377	0.31	5.00
13	“	7.59	2.27	40	0.347	0.385	0.37	4.91
14	$Bi(NO_3)_3$	1.74	1.21	40.7		0.426	0.45	4.44
15	“	2.35	1.65	40.9		0.582	0.75	4.32
16	“	2.87	2.01	41.1	0.716	0.717	1.04	4.35

It will be seen that the contents of most of the bottles had come to equilibrium, but Nos. 11, 12, and 13 were still changing. Nos. 1 to 10 had solid contents of constant composition in equilibrium with liquids of different concentrations, and these, therefore, contained but one solid phase, $6Bi_2O_3.5N_2O_5$. Nos. 14 to 16 also contained one solid phase, $BiONO_3$. Nos. 11 to 13 contained the salt $BiONO_3$ partially converted into the salt $6Bi_2O_3.5N_2O_5$, but, as equilibrium had not been reached, the liquid phase was not of constant concentration.

A quantity of the salt $6Bi_2O_3.5N_2O_5$ was prepared by stirring the salt $BiONO_3$ with water, care being taken that the mother-liquor was of a concentration found by the previous experiment to be in equilibrium with that compound. This was used in some of the bottles in the next series. A higher temperature was now used in order that more basic nitrates might be obtained, and, also, that equilibrium might be more quickly reached.

Table C.

Temp. 50°. $\frac{Bi_2O_3}{N_2O_5}$ in $2Bi_2O_3.N_2O_5 = 8.63$.

No.	Salt used.	Components used.			Acidity of liquid.			Bi_2O_3 in solution. Grams.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
		Bi_2O_3. Grams.	N_2O_5. Grams.	H_2O. cc.	6 days. N.	13 days. N.	19 days. N.		
1	$6Bi_2O_3.5N_2O_5$	1.53	0.295	40.2	0.057	0.056	0.057	....	8.74
2	"	2.30	0.443	40.3	0.080	0.080	0.081	....	8.59
3	"	3.06	0.590	40.4	....	0.109	0.108	....	8.50
4	"	3.83	0.730	40.5	1.36	....	0.135	0.03	8.63
5	"	4.60	0.873	40.6	1.60	0.159	0.159	0.04	8.64
6	"	6.12	1.164	40.9	....	0.217	0.216	0.07	8.76
7	"	7.66	1.451	41.1	....	0.265	0.265	0.11	8.67
8	"	9.20	1.75	41.3	0.275	0.284	0.286	0.13	8.09
9	"	11.49	2.18	41.6	0.270	0.284	0.283	0.13	7.33
10	"	15.32	2.90	42.2	0.235	0.270	0.276	....	....
11	$BiONO_3$	3.79	0.88	40	0.075	0.242	0.251	....	....
12	"	7.59	1.75	40	0.144	0.193	0.286	0.13	6.27
13	"	11.38	2.63	40	0.216	0.217	0.215	0.08	(5.20)
14	"	15.18	3.51	40	....	0.286	0.284	0.13	5.18
15	"	11.38	2.63	25	....	0.350	0.352	0.17	5.20
16	"	15.18	3.51	25	....	0.467	0.466	0.22	5.17

In this series, Nos. 1 to 7 contained one solid phase, $2Bi_2O_3.N_2O_5$, and Nos. 14 to 16 also contained one solid phase, $6Bi_2O_3.5N_2O_5$. Nos. 8, 9, and 12 were a monovariant system and contained varying proportions of the salts $2Bi_2O_3.N_2O_5$ and $6Bi_2O_3.5N_2O_5$ in equilibrium with liquids of the same composition, as we may neglect the possibility of this being the temperature and concentration at which a nonvariant system can exist. In Nos. 10, 11, and 13, at the first analysis, the solid contents had changed from the form $BiONO_3$ to the form $6Bi_2O_3.N_2O_5$, and the reaction seems to have halted there. They were then seeded with the salt $2Bi_2O_3.N_2O_5$ and, at the end of thirteen days, the reaction had proceeded further in Nos. 11 and 12, but in No. 13 further action had not begun in nineteen days. The same result was observed if the experiment was begun with one of the basic nitrates, and a solution of nitric acid instead of water. No reaction took place for days, the length of time before the reaction began depending on the concentration of the nitric acid.

A series of experiments was begun at 75°, but only three measurements were obtained, as all the other bottles broke at that temperature.

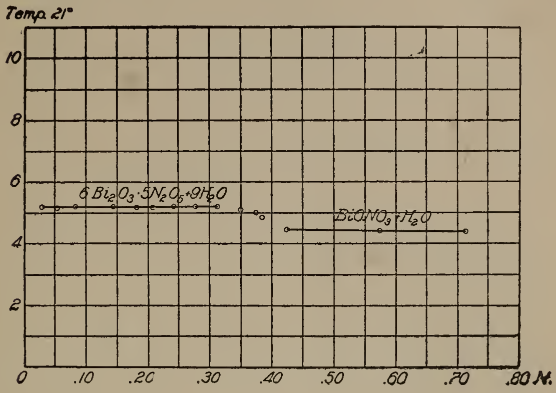
Table D.

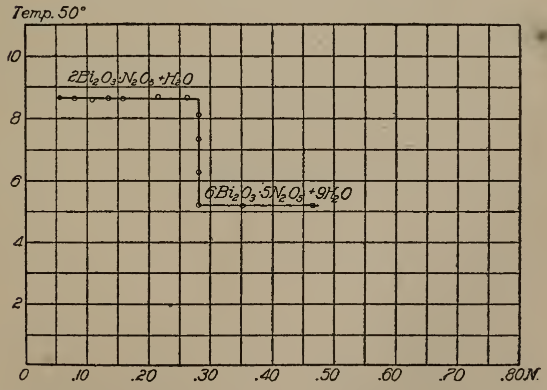
Temperature 75°.

No.	Salt used.	Components used.			Acidity of liquid, 2 days.	Bi_2O_3 in solution.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
		Bi_2O_3. Grams.	N_2O_5. Grams.	H_2O. cc.	N.	Grams.	
1	$6Bi_2O_3.5N_2O_5$	3.06	0.59	40.4	0.109	0.03	8.65
2	"	6.13	1.16	40.9	0.208	0.05	8.68
3	"	9.19	1.75	41.3	0.314	0.15	8.61

If we represent the results given in Tables *B* and *C* in diagrams taking as abscissae the concentration of nitric acid in the liquids in the different bottles expressed in terms of a normal solution, and as ordinates the relation between bismuth oxide and nitric anhydride in the solid contents, horizontal lines represent divariant systems consisting of one solid, a liquid, and a gas, and perpendicular lines represent monovariant systems consisting of two solids, a liquid and a gas. The concentration of the gaseous phase is a function of the concentration of the liquid. In the diagram representing

Table *B* there is no perpendicular line because equilibrium had not been reached in the bottles whose contents are represented between the two horizontal lines.





The solid contents in Nos. 1 to 7, Table *C*, and also those in Nos. 14 to 16 in the same series, were filtered off and dried between filter-paper. An analysis of these two products gave the following results :

	Calculated for $6Bi_2O_3.5N_2O_5 + 9H_2O =$ $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$.	Found.
Bi	71.65	71.70
NO_3	17.77	17.81

	Calculated for $2Bi_2O_3.N_2O_5 + H_2O =$ $Bi_4O_5(NO_3)_2 + H_2O$.	Found.
Bi	78.97	78.86
NO_3	11.76	11.80

Both were impalpable white powders and neither lost in weight when heated for some hours at 100°.

Conclusions.

1. Pouring nitric acid solutions of bismuth into water at ordinary temperature gives only the salt $BiONO_3 + H_2O$ if the precipitate be quickly filtered off, even when the resulting mother-liquor is such as is in equilibrium only with a more basic nitrate. This is due to the fact that where the strong acid solution meets the water and the salt $BiONO_3 + H_2O$ is formed, the concentration of the acid is high, and when the crystalline precipitate comes in contact with the weaker acid the reaction is too slow to produce an appreciable change in a few hours.

2. At 21°, the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ is in equilibrium with nitric acid solutions from 0.03 to 0.32 normal, and the salt $BiONO_3$ with solutions from 0.425 to 0.72 normal.

3. At 50°, the salt $Bi_4O_5(NO_3)_2 + H_2O$ is in equilibrium with nitric acid solutions from 0.057 to 0.285 normal, and the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ with solutions from 0.285 to 0.466 normal.

4. At 75°, the salt $Bi_4O_5(NO_3)_2 + H_2O$ is in equilibrium with solutions of nitric acid from 0.109 to 0.314 normal.

5. That no basic nitrate containing a greater proportion of nitric anhydride than the salt $Bi_4O_5(NO_3)_2 + H_2O$ and less than the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ exists at 50°, although at least two were said to have been prepared at that temperature.

6. That the slowness of the reaction, or a concentration of the mother-liquor at which a monovariant system was possible, accounts for the many basic nitrates which have been described.

7. That reaction between the higher basic nitrates and water containing nitric acid begins only after some time.

THE CHEMICAL LABORATORY OF
THE UNIVERSITY OF TORONTO,
January, 1901.

A NEW TEST FOR CHLORINE FOR USE WITH THE BLOWPIPE.

BY HENRY W. NICHOLS.

A piece of absorbent paper moistened with a solution of cobalt chloride turns blue when warmed.

A piece of absorbent paper moistened with a solution of cobalt bromide or iodide turns green when warmed.

A piece of absorbent paper moistened with a solution of cobalt nitrate turns a deeper rose color and darkens when warmed.

Paper moistened with solutions of other cobalt salts, when dried in the air, does not turn either green or blue at a temperature below that of the carbonization of the paper.

Paper moistened with a solution of cobalt nitrate and a soluble chloride acts upon warming as if it were moistened with cobalt chloride.

Upon these facts is based the following test for chlorine and for the distinction between chlorine and bromine or iodine. This test calls for such apparatus and reagents only as are commonly used in blowpipe work :

Powder the assay with from one to four volumes of potassium bisulphate. Place the mixture in a closed tube. Moisten a fragment of filter-paper with cobalt nitrate solution and place it in the mouth of the tube. Upon fusing the mixture, the paper under the influence of the hydrochloric acid and sulphuric anhydride given off will turn a bright blue if chlorides are present. If bromides or iodides are present the color will be green. In case of minute quantities it may be necessary to dry the paper before the color appears but ordinarily the sulphuric anhydride evolved by the bisulphate produces the same effect as heating. Although the blue of the cobalt chloride assumes, when faint, a greenish cast, yet it is always distinct from the yellowish-green of bromides. When chlorides and bromides are found together, the paper turns first blue from chlorine and later green from bromine. If but little bromine is present the final color will be a bluish-green. The test is much less delicate for bromides than for chlorides. If but little chlorine is present and much water condenses in the tube, this water may hold back the hydrochloric acid and should be driven into the test paper. When this occurs it is often necessary to heat the paper to bring out the color, and under these conditions the yellow of the charred paper may produce with the blue a green, somewhat similar to that produced by bromides. Acid potassium sulphate, as purchased, contains too much sulphuric acid and should be fused in platinum until frothing ceases before use; otherwise it froths in the tube in a disagreeable manner. Many bromides contain sufficient chlorine to give a distinct test by this method, a fact that should be remembered when using them for check experiments. The limit of sensitiveness of the test has not been determined. The following tests will indicate its suitability for blowpipe work and mineral determinations: Two specimens of embolite were tested and both the chlorine and bromine were indicated. A specimen of sodalite (Cl, 7.3 per cent) gave a good reaction for chlorine, as did a specimen of zunyite (Cl, 2.91 per cent) with about 25 per cent of gangue. The white crystalline apatite of Snarum, Norway, gave a good reaction while a specimen of the green massive Canadian apatite gave no reaction for the traces (0–0.5 per cent) it generally carries.

Chlorides in solution may be tested by dipping a paper into the solution, spreading a drop of cobalt nitrate solution upon it, drying, and heating. The test thus carried out is not very delicate; moreover, the distinction between chlorides and bromides is obscured, and sulphides and some other substances interfere.

The familiar test for chlorine in the presence of bromine by the generation of chlorochromic anhydride may be advantageously modified for the blowpipe laboratory. In place of the tubulated test-tube a plain test-tube may be used, and in place of the receiver a piece of filter-paper moistened with a saturated solution of sodium carbonate and placed in the mouth of the tube. This alkaline paper retains chromic acid so that when burned in the forceps the ash will give a chromium reaction with the borax bead. No difficulty will be found in burning the paper while moist, owing to the bromates and chromates present. During the burning the sodium carbonate fuses and collects the ash into a globule which will be a dirty green if it contains much chromium. For the small quantities of material commonly used in mineral testing, a closed tube may be very advantageously substituted for the test-tube whenever the substance tested does not effervesce with acid.

FIELD COLUMBIAN MUSEUM,
February 12, 1901.

ON TRIVALENT CARBON.

(REPLY TO J. F. NORRIS.)

BY M. GOMBERG.

The January number of this JOURNAL[1] contains a paper by Norris and Sanders on "Triphenylchlormethane." They describe a method for the preparation of this compound, which is essentially the same as that published by me some two months previously.[2] Although my paper was presented in full at the Columbus meeting of the American Association for the Advancement of Science, it was given in the Proceedings only by title. This is undoubtedly the reason why the paper escaped the notice of Norris and Sanders before this subject was taken up by them.

In another place[3] I reported the study of the action of metals upon triphenylhalogenmethanes. It was shown in that paper that when silver, mercury, or zinc is allowed to act at ordinary temperature upon triphenylchlor- or brommethane in different solvents, in absence of oxygen, the halogen is removed quantitatively, and there results an extremely unsaturated compound, which, on exposure to air, at once becomes oxidized. The reactions of the resulting oxygen derivative led me to the conclusion that it is best represented by the formula $(C_6H_5)_3C—O—O—C(C_6H_5)_3$; *i.e.*, peroxide of triphenyl-

---

[1] This JOURNAL, **25**, 54.

[2] ~~*Ibid.*~~, **22**, ~~750.~~

[3] ~~*Ibid.*~~, **22**, 757.

20–25

Jr. Amer Chem Soc

methyl, while the unsaturated hydrocarbon was assumed to be triphenylmethyl itself, $(C_6H_5)_3C$—, wherein carbon is trivalent.

On p. 58 Norris and Sanders state that metallic sodium has no action on triphenylchlormethane dissolved in ether. On the addition of brombenzene to the solution a reaction took place, and one of the products isolated, while containing no halogen, did not, on analysis, give a sum of carbon and hydrogen equal to 100 per cent. It does not appear quite clear how they "have discovered that an oxygen compound was formed as the result of the action of sodium on a mixture of triphenylchlormethane and brombenzene." This oxygen compound might as well have been the result of the action of *sodium hydroxide*, which was undoubtedly formed to some extent during the three days required for the reaction. Complete exclusion of oxygen-bearing reagents, of the atmospheric oxygen itself, and the subsequent oxidation of the resulting hydrocarbon,—were the proofs necessary to establish the discovery. Nothing of this is mentioned in their paper. They say that this substance resembles the peroxide described by me in melting-point, chemical composition, and solubility, "but further work is necessary before the identity of the two substances can be established." In the second paper[1] not a word is said with reference to this further work. Norris speaks of the oxygen compound as identical with the peroxide described by me. The formation of that body is self-evident in the light of the results published by me. It seems, therefore, strange that Norris should at this stage give up his original problem, the synthesis of tetraphenylmethane, and take up the study of the action of metals upon triphenylchlormethane. I have published only a preliminary paper upon this subject, asking that the field might be reserved for myself. Norris states in the first paper that his problem, while it has a bearing upon my work, is in itself quite distinct. And yet, his whole second paper is devoted to a repetition of my experiments on the action of zinc upon triphenylchlormethane. In my preliminary paper the metals mentioned were sodium, silver, mercury, and zinc; the solvents, benzene, carbon disulphide, and carbon tetrachloride. But, of course, other solvents and other metals have been tried before and since the publication of the paper. During the past few months particular attention has been paid to this reaction both in ether and acetic ether as solvents. As my results are entirely different from those obtained by Norris, I publish some of them at this time.

---

[1] This JOURNAL, 25, 117.

At the early stage of this work, absolute ether was frequently employed as a solvent in the reaction of metals upon triphenylhalogenmethane. But, as the substance obtained was shown to contain oxygen, ether was discarded for liquids which do not contain oxygen. It was afterwards shown that the formation of the oxygen derivative does not depend upon the oxygen of the ether, and it was demonstrated that whatever the solvent may be, the reaction is always the same,—the metal removing the halogen from triphenylchlormethane and giving as a result a highly unsaturated hydrocarbon; this was instantly oxidized to an insoluble oxygen compound on exposure to air. The ease with which ether can be removed at low temperatures induced me again to use it in this reaction, with the hope of obtaining the pure, free hydrocarbon. But I noticed that while the reaction proceeded smoothly in many trials, in some instances a dark, thick mass would separate, and in several cases, when zinc was employed, a gas was given off. It was, however, finally shown that the evolution of hydrogen was due to the presence of traces of alcohol or water in the ether. With absolutely dry ether no gas was developed, and by use of this solvent I obtained the triphenylmethyl in large transparent crystals which, on analysis, gave carbon and hydrogen, 99 per cent. Ethyl acetate behaves exactly like ether, but possesses the great advantage that it keeps the zinc chloride formed during the reaction in solution. All the results obtained by Norris are due to the fact that the ethyl acetate employed by him was not pure, and they have no direct bearing upon the question of the valency of carbon.

I. Is Hydrogen Formed in this Reaction?

a. The action of zinc in ethyl acetate.—The ethyl acetate was purified in the following way: The ester (Kahlbaum) was shaken with a solution of sodium carbonate to remove the acetic acid, and the clear filtrate was allowed to stand for twenty-four hours over a third of its bulk of granulated calcium chloride. It was then distilled and the fraction boiling at 75° to 77° C. was collected separately. This fraction was heated on the water-bath for three hours with phosphorus pentoxide,[1] 100 grams to a liter of the ester. The ethyl acetate was then decanted upon a fresh charge of phosphorus pentoxide and heated for two hours. The liquid was then decanted and distilled. Nearly all came over at the temperature of 76°.4 to 76°.8 C., and the solvent was then fit to be used. Although zinc in any form can be used for this reaction, it is preferable, as will be seen below, to use zinc strips cut of the desired size from ordinary zinc sheet. Strips of about 0.5 x 3 inches are most convenient. The zinc is freed from oxide either by dilute sulphuric acid, or by means of a file or emery paper.

If triphenylchlormethane (1 gram) is dissolved in about 10 cc. of ethyl acetate purified as described above, and the air in the test-tube is displaced by carbon dioxide, then, on dropping in the strip of zinc and rapidly inserting the stopper, the following will be observed: The solution will immediately turn yellow and in a few minutes crystals, which rapidly grow both in size and in number, will appear on the zinc. These large, transparent, pale-yellow crystals are triphenylmethyl itself. This substance, just as in ether, is only slightly soluble in ethyl acetate. Not a bubble of gas will be seen to rise to the surface. I have had occasion to perform this experiment over fifty times with small and large quantities, with both absolute ether and acetic ether, watching the metal for hours through a magnifying glass, and am satisfied that when all the reagents are pure and dry no gas is generated. A solution of these crystals in benzene or in carbon disulphide will rapidly decolorize iodine. On exposure to air the peroxide will be formed. These results, obtained with triphenylmethyl, will be reported later.

The following series of experiments, which were carried out under as nearly the same conditions as possible, show the necessity of employing pure reagents in this reaction. The triphenylchlormethane used was recrystallized from absolute ether and kept in a desiccator provided with soda-lime and sulphuric acid, and in this way was kept free from moisture and hydrochloric acid. In each case 1 gram of the halogen compound was dissolved in 15 cc. of acetic ester placed in a small Erlenmeyer flask provided with a stopper and a calcium chloride tube about 4 inches long. A strip of zinc was then introduced into the solution. The unsaturated hydrocarbon which was formed under these conditions was instantly oxidized to the insoluble peroxide by the dry air entering through the calcium-chloride tube. Occasional shaking facilitates the speed of the oxidation. After a few hours' standing the peroxide was filtered off and thoroughly washed with ether and alcohol. The small amount of the substance adhering to the zinc was scraped off with a spatula, digested with dilute hydrochloric acid, and added to that already collected. The whole precipitate was then washed with dilute acid, water, alcohol, and ether, and dried. As the peroxide is only very slightly soluble in acetic ester and in the other solvents used in this operation, no attempt was made to recover the small amounts lost in this way. The loss amounted to about 25 milligrams. The peroxide was in all cases quite pure, melting at 182° to 185° C.

---

[1] P. C. Freer: This JOURNAL, 13, 310.

(1) One gram of triphenylchlormethane, treated as above described in the pure and dry ethyl acetate, gave 0.705 gram of the peroxide. No hydrogen was given off.

(2) Some of the pure ester was shaken with a solution of sodium carbonate, and the clear liquid filtered through a dry filter. The ester was now in the same condition as used by Norris. One gram of the chlorine compound was dissolved in 15 cc. of this solvent. The zinc was at once attacked with strong evolution of hydrogen, but the yield of the peroxide was only 0.050 gram.

(3) Moist ethyl acetate was dried over calcium chloride for one hour. This time the evolution of hydrogen was decidedly less, and the yield of the peroxide was 0.195 gram.

(4) Acetic ester was dried over calcium chloride for five hours. In this case the evolution of gas did not begin till some ten minutes after the introduction of the zinc. It then

proceeded slowly for quite a long time. There is no difficulty in distinguishing, by means of a magnifying glass, the rapidly rising bubbles of gas from the small shining crystals of the peroxide floating through the liquid. The yield of the peroxide was 0.485 gram.

(5) The ester was allowed to stand over one-half its bulk of granulated calcium chloride for twenty hours, and then for five hours longer over a fresh charge of fused calcium chloride. No hydrogen was given off, not a bubble of gas could be noticed, and yet the yield of the peroxide was only 0.550 gram.

(6) The ester from the previous experiment was then treated with phosphorus pentoxide and distilled. Again no hydrogen was formed, but the yield of the peroxide rose to 0.730 gram.

(7) To 15 cc. of the perfectly dry ester 0.1 cc. of absolute alcohol was added. While there was no hydrogen given off the yield of the peroxide showed plainly that the chlorine compound was etherified. The yield was only 0.325 gram. With an ester containing 0.1 per cent alcohol there is an unmistakable evolution of hydrogen.

These results show, it seems to me, quite conclusively that the generation of hydrogen and the formation of the peroxide are not the consequences of one and the same reaction. On the contrary, they are antagonistic to each other; the quantity of one is inversely proportional to that of the other. If, as Norris supposes,[1] the action of metals upon triphenylchlormethane results in the splitting off of hydrochloric acid, and this by its action upon the metal furnishes hydrogen, then the amount of the gas evolved should be proportional to the quantity of the unsaturated hydrocarbon, and consequently to that of the peroxide. But what actually happens is the very opposite. As the increase of the amount of hydrogen and the corresponding decrease of the peroxide seem to depend upon how dry the solvent is, the explanation of what happens is this: The chlorine compound is a very unstable body and is easily decomposed by water. When dissolved in ethyl acetate containing some water, it is partially hydrolyzed into triphenylcarbinol and hydrochloric acid, and the latter attacks the zinc. When alcohol is present in the ester, etherification instead of hydrolysis takes place :

---

[1] A similar theory was advanced by Nef (Ann. Chem. (Liebig), 309, 167) before the publication of my first paper upon this subject.

$$(C_6H_5)_3C.Cl + H_2O = (C_6H_5)_3C.OH + HCl\,;$$
$$(C_6H_5)_3C.Cl + C_2H_5.OH = (C_6H_5)_3C.OC_2H_5 + HCl.$$

Nor is it necessary to assume that these changes are instantaneous. The hydrolysis may be only partial, depending upon the relative proportions of water and of the chlorine compound. The equilibrium so established is, however, disturbed as soon as zinc is introduced. As the hydrochloric acid is being used up by the metal, the hydrolysis proceeds further and further. It is evident that the more water there is present in the ester, the more rapid and the more complete is the hydrolysis, and consequently the less peroxide will be formed. Experiments (5) and (7) also show that the acid produced may be too dilute to act upon the zinc at all.

The readiness with which the chlorine compound is hydrolyzed is shown by the following experiment: If absolutely dry halogen compound is dissolved in absolute ether, dry acetic ester, or dry benzene, and a strip of blue litmus paper is introduced into each solution, it will be but a few minutes before the litmus will begin to show an acid reaction. It will turn red, first in the benzene, then in the ether, and last in the ethyl acetate. Apparently there is enough water in the paper to affect the triphenylchlormethane. Hence the acid reaction obtained by Norris[1] in treating the chlor-compound with zinc in moist acetic ester is not at all an indication that hydrochloric acid is split off by the action of the metal.

An attempt was made to measure the degree of hydrolysis by determining the electrical conductivity of the resulting hydrochloric acid. But the acetic ester, like a great many other organic solvents, is almost a perfect non-conductor. The purified and dried ester showed no electrical conductivity when tested with the apparatus at my command.[2] When shaken with a solution of sodium carbonate and filtered through a dry filter, the moist ester also did not show any measurable conductivity. A dilute solution of dry hydrochloric acid in dry ethyl acetate, tested as to its conductivity, gave entirely negative results, and yet this solution attacked zinc very readily. To 15 cc. of the dry ester 1 drop of concentrated hydrochloric acid was added; even this solution, although containing traces of water, presented such enormous resistance that its conductivity could not be measured until another drop of water was added. This solution also acted upon zinc with evolution of hydrogen. One-half gram of triphenylchlormethane was dissolved in 10 cc. of the dry ester; no measurable electrical conductivity could be noticed, and the solution gave no hydrogen on the addition of zinc. One-half gram of the halogen compound was dissolved in moist ethyl acetate which had been previously shaken with a solution of sodium carbonate. The solution showed a conductivity of about 0.5×10^{-6}; zinc was acted upon by the solution and hydrogen was formed. A solution of the same concentration in acetic ester which had been dried over calcium chloride only two hours showed no electrical conductivity, but still gave hydrogen when zinc was added. The results from all these experiments show plainly that the amount of hydrochloric acid in ethyl acetate cannot be measured by the degree of the conductivity of the solution; they also show that more than a mere trace of water must be present in order that there should be a measurable conductivity. It is also seen that the readiness of chemical action upon zinc is not at all parallel to the conductivity of the acid in this solvent. Kablukoff[1] showed that the conductivity of hydrochloric acid in dry benzene, xylene, hexane, and ether is very slight. Zecchini[2] has recently shown that dry hydrochloric acid in methyl, ethyl, and amyl alcohol, in acetone, and in ether acts energetically upon zinc; best of all in ether. Apparently the degree of chemical action in these instances is not parallel to that of dissociation; or, perhaps, the conductivity is not in these solvents a reliable measure of dissociation.[3]

---

[1] This JOURNAL, **25**, 120.

[2] I used a Kohlrausch apparatus with a 20,000 ohm resistance, and no minimum was obtained.

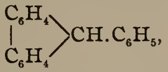
---

[1] Ztschr. phys. Chem., 4, 429.

[2] *Ibid.*, 27, 186.

[3] It may be concluded from Experiment 4 that small amounts of hydrochloric acid in tolerably dry ethyl acetate can be detected by the action upon zinc when the electrical conductivity method will fail. Experiment 5 shows that the relative yield of the peroxide is even a more delicate test for the partial hydrolysis of the triphenylchlormethane than the test with zinc.

Norris thinks it probable that, when zinc reacts with triphenylchlormethane, the metal causes the elimination of hydrogen chloride and not that of chlorine alone. Such a loss of hydrogen chloride, according to him, has already been observed, and he cites the experience of Hemilian.[1] Now, E. and O. Fischer[2] proved that when pure triphenylchlormethane is used, Hemilian's diphenylenephenylmethane,



$$\left.\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\right\rangle CH.C_6H_5,$$

is formed only in minute quantities, if at all. It is only when the chlorine compound contains a considerable quantity of the carbinol that the hydrocarbon in question is produced. Neff[3] came to the same conclusion when triphenylbrommethane is substituted for the chlorine compound. Then again, the temperature of formation, 250° C., precludes any parallelism between Hemilian's reaction and that of the action of metals at ordinary temperatures. E. and O. Fischer justly conclude that Hemilian's body is not the result of a simple molecular rearrangement, but rather that of a very complicated decomposition. Indeed, the temperature is of very great importance in the action of metals upon triphenylhalogenmethane, as is shown by Nef's results.[4] Nef heated triphenylbrommethane in absolute ether with sodium, zinc, and mercury at 60° to 150° C. and obtained a mixture of products, but not triphenylmethyl.

b. The action of zinc in benzene.—When zinc acts upon triphenylchlormethane in benzene no hydrogen is given off. This has been confirmed by Norris. But Norris is of the opinion that the nascent hydrogen in this instance is taken up by the benzene, the latter forming additive products. In support of this view he cites the following experiment: "Sodium was added to ether which contained a small quantity of water, and the amount of hydrogen evolved was noted. Some benzene was now added. The evolution of gas was reduced to almost one-half."[5] It is, however, well known that of all the aromatic compounds benzene itself is as difficult to reduce as any. Hexahydrobenzene could only be obtained when benzene is heated with a large quantity of hydriodic acid (1.96) at 280° C.[1] Tetrahydrobenzene is not known at all. Dihydrobenzene was obtained by Baeyer[2] from dibromhexamethylene. Why, then, in this action of zinc *all* the hydrogen should be taken up by the benzene does not appear from Norris's experiments. But is it not possible that in Norris's experiment the decrease of the amount of hydrogen simply indicates a retardation of the action of water upon the sodium? On the addition of benzene to ether containing sodium the latter soon gets coated with a gelatinous, transparent layer which protects it from further action. If a fresh piece of metal is now added, the evolution of hydrogen will once more begin, and will continue until this new piece also becomes coated. A fresh addition will once more start the evolution, etc.

---

[1] Ber. d. chem. Ges., 7, 1208.

[2] Ann. Chem. (Liebig), 194, 259.

[3] Ann. Chem. (Liebig), 309, 168.

[4] *Ibid.*, 309, 169.

[5] This JOURNAL, 25, 121.

I cannot agree with Norris that the action of zinc in benzene is much slower than in other solvents. Norris worked with 1 gram, while the experiments described by me referred to 20 grams of the triphenylchlormethane. Norris simply desired to show that a reaction takes place when ethyl acetate is substituted for benzene, while my object was to show that the abstraction of halogen is quantitative. Hence I thought it best to allow the solution to stand at least five days to insure complete change; but when zinc dust is used with a gram of the material the reaction can be brought to an end in a very short time.

c. Action of mercury on benzene.—The following experiments show conclusively, I believe, that the action of metals does not cause the elimination of hydrochloric acid.

(1) A solution of dry hydrochloric acid in dry benzene was prepared. The strength of the solution was found by shaking 20 cc. of the latter with a solution of silver nitrate and estimating the resulting silver chloride. Ten cc. of the benzene were found to contain 0.0446 gram of the acid. Twenty cc. of this solution were placed in a small Claisen distilling flask,

---

[1] Wreden: Ann. Chem. (Liebig), **187**, 163.

[2] Ber. d. chem. Ges., **25**, 1840.

which was connected with a drying tube and a receiver containing a solution of silver nitrate. Fifty grams of mercury were then added, and the flask was allowed to stand several hours, the mixture being shaken occasionally. A stream of dry carbon dioxide was then passed through the solution and the hydrochloric acid not taken up by the metal was in this way driven over into the receiver. The quantity thus recovered was 0.0862 gram. As is seen from this, only 3 mgs. of the acid combined with the mercury under these conditions.

(2) Two grams of triphenylchlormethane were dissolved in 20 cc. of dry benzene, which contained no acid, the solution was placed in a dry Claisen flask, connected as before with a receiver containing a solution of silver nitrate. Fifty grams of mercury were added and the mixture was allowed to stand several hours. A stream of perfectly dry carbon dioxide was then passed through the solution for twenty-four hours. The silver nitrate solution showed at the end of that time only a slight turbidity, and yet the filtered benzene solution furnished on exposure to air 0.9 gram of the triphenylmethyl peroxide. Had the metal caused elimination of hydrochloric acid from the halogentriphenylmethane, there should have been formed in this experiment 0.1278 gram of the acid. It was shown above that mercury was only slightly attacked by hydrochloric acid in benzene; consequently, had there been any hydrochloric acid formed in this experiment at all, a large amount of it should have been found in the receiver.

(3) The question may well be asked, whether the chlortriphenylmethane or the resulting triphenylmethyl, does not exert some catalytic influence, causing the hydrochloric acid to act upon the mercury. In order to test the theory, the experiment described under (2) was repeated, substituting, however, benzene containing hydrochloric acid for the pure solvent. Of the 0.0892 gram of acid introduced, 0.0822 gram was found in the receiver, as compared with 0.0862 gram obtained in the blank experiment (1). The loss of the 0.004 gram of the acid is easily accounted for by the more finely divided state of the mercury caused by a change in the surface-tension of the metal. A somewhat larger surface was exposed and the action of hydrochloric acid proceeded

with a proportionately greater velocity. The benzene solution gave on exposure to air 1 gram of the peroxide, which should have been accompanied by 0.142 gram of hydrochloric acid. Yet none of this additional acid was found in the receiver. No doubt, none was formed.

d. Action of concentrated sulphuric acid.—The action of concentrated sulphuric acid upon triphenylchlormethane is also considered by Norris as a proof that the metal causes the elimination of hydrochloric acid from the halogen compound, and not that of halogen alone. He found that on dissolving triphenylchlormethane in concentrated sulphuric acid large quantities of hydrochloric acid are given off. The observation is correct, but there is no analogy between this reaction and that of metals upon the halogen compound. Benzalchloride and benzotrichloride react with sulphuric acid with the evolution of hydrochloric acid, and the acid sulphates so formed are easily hydrolyzed. This forms the basis of the patented methods for the manufacture of benzaldehyde and benzoic acid.[1] The reaction in the case of triphenylchlormethane is no doubt perfectly analogous, being probably this:

$$(C_6H_5)_3C.Cl + H_2SO_4 = (C_6H_5)_3C.OSO_3H + HCl\,;$$
$$(C_6H_5)_3C.OSO_3H + H_2O = (C_6H_5)_3C.OH + H_2SO_4.$$

One gram of the halogen compound was dissolved in 10 cc. of sulphuric acid, and the clear yellow solution was poured into water. The snow-white, flocculent triphenylcarbinol thus obtained melted at 154° to 158° C. 0.925 gram was obtained in this way, while the theoretical quantity is 0.934 gram, making a yield of 99 per cent. This may prove to be the best method for the preparation of triphenylcarbinol.

II. Does Dry Oxygen Give the Peroxide?

It is known that certain chemical reactions do not take place when all traces of water are completely excluded. Some assume that slow oxidation by the atmospheric oxygen also requires at least traces of moisture. Traube's theory, that oxidation in general is never effected directly by molecular oxygen, but always through the intervention of water, is also accepted by Nef. Nef[1] could not oxidize dry benzaldehyde to benzoic acid by perfectly dry oxygen. Jorissen,[2] however, could not confirm these results. Engler and Weisberg[3] succeeded in oxidizing turpentine when all possible traces of moisture were rigidly excluded. Whichever theory is accepted as to the part that water plays in all cases of slow oxidation, or *autoxidation*, one fact is established beyond any doubt: *molecular* oxygen never oxidizes water to hydrogen peroxide, a substance which has been shown to occur in a large number of instances of autoxidation of metals and of many organic compounds. The different theories which attempt to explain its formation—those of Schönbein, Traube, and Engler—all agree on this point: It is never the result of the direct oxidation of water by the molecular oxygen. According to Norris, the unsaturated hydrocarbon, which is formed by the action of zinc upon triphenylchlormethane, has the constitution $(C_6H_5)_2C:C_6H_4$. Such a body could, he states, give rise to the peroxide,

---

[1] V. Meyer and P. Jacobsen: Lehrbuch, II, pp. 479 and 537.

$$(C_6H_5)_3C{-}O{-}O{-}(C_6H_5)_3C,$$

by the combined action of oxygen and water, or by the action of hydrogen peroxide; hence water is absolutely necessary for this reaction. But then, the water cannot form hydrogen peroxide unless the hydrocarbon itself is first oxidized directly by the atmospheric oxygen, a part of which becomes in this way what is known as "active" oxygen, and is then capable of oxidizing water or some other "acceptor." The reaction must be represented as follows:

$$\text{Hydrocarbon} + (O{=}O) + H_2O = (\text{Hydrocarbon} + O) + H_2O_2 \text{ (I)}.$$

The hydrogen peroxide in its turn gives rise to the reaction:

$$2(C_6H_5)_2C:C_6H_4 + H_2O_2 = (C_6H_5)_3C{-}O{-}O{-}(C_6H_5)_3C \text{ (II)}.$$

We thus reach the conclusion that if hydrogen peroxide causes the formation of triphenylmethyl peroxide (II), the necessary hydrogen peroxide can only result from a direct oxidation of another portion of the unsaturated hydrocarbon by the atmospheric oxygen (I). But it was shown above that the yield of the triphenylmethyl peroxide is 80 per cent of the theoretical quantity. Consequently, the remaining 20 per cent must have taken up a quantity of oxygen equal to that which combined with the water to form the hydrogen peroxide for the use of the remaining 80 per cent of the hydrocarbon. In other words, there ought to be formed in addition to the insoluble triphenylmethyl peroxide another product very much richer in oxygen, supposing even that all the hydrogen peroxide is used up in the formation of the triphenylmethyl peroxide. I have been at work for some time trying to determine what becomes of the remaining 20 per cent of the triphenylmethyl. I find some triphenylmethane, some triphenylcarbinol, and a portion which cannot be brought to crystallization. It remains, however, to determine whether all these products are formed before or during the oxidation of the unsaturated hydrocarbon.

---

[1] Ann. Chem. (Liebig), 298, 280.

[2] Bodländer: "Ueber langsame Verbrennung," p. 83.

[3] Ber. d. chem. Ges., 31, 3049.

But aside from the theoretical considerations it is not difficult to prove experimentally that the hydrogen peroxide theory, or even the simple theory of the combined action of oxygen and water, is not correct. The reaction,

$$2(C_6H_5)_2C:C_6H_4 + H_2O + O = (C_6H_5)_3C—O—O—C(C_6H_5)_3,$$

implies that a certain quantity of water must be used up in the formation of the peroxide. The production of 1 gram of the peroxide represents a disappearance of 0.0354 gram of water. This is certainly a weighable amount, and can be excluded if desired. Accordingly, Norris was unable to obtain the peroxide when dry air was drawn through a benzene solution of the compound for twenty minutes. I have had occasion to make the peroxide a great many times, and have never failed to get it by the use of air which was passed through a drying train such as is used in elementary analysis. The comparative yields of the peroxide with moist and dry ethyl acetate as a solvent were obtained, it will be remembered, by the use of dry air. The following experiments, however, show conclusively that water does not enter into the reaction as such :

Three grams of pure and dry triphenylchlormethane were dissolved in ethyl acetate which had been thoroughly dried over phosphorus pentoxide and placed in a small Drechsel bottle (Fig. 1). The joint in the neck was carefully ground

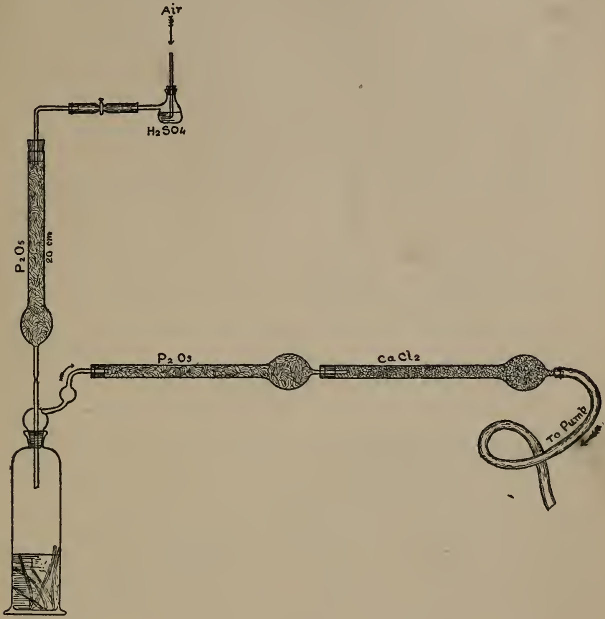


Fig. 1.

and was shown to be air-tight. The apparatus was first dried by heating it with a naked flame and exhausting, and then allowing air, which was passed in a slow stream through sulphuric acid and phosphorus pentoxide, to enter the flask. This treatment was repeated ten times. The solution of the halogen compound and a few strips of zinc were then introduced. The reaction began at once, and no evolution of hydrogen could be detected. A slow stream of dried air was passed over the solution from the very beginning of the reaction by means of a suction pump, care being taken to prevent backward diffusion of moisture as shown in the sketch. The triphenylmethyl peroxide began to form at once, and the precipitate kept on increasing as the reaction proceeded. After a day's action 2.050 grams were obtained, which is 73 per cent of the theoretical amount. The experiment was repeated with 5 grams, and this time the air was passed into the solution of the halogen compound. The yield was 3.650 grams, which is 78.5 per cent of the theoretical quantity. In this last instance there should have been used up 0.128 gram of water, which is far from a negligible quantity, and was certainly excluded by the conditions of the experiment.

It might be said that perhaps the zinc chloride formed in the reaction causes a condensation of some acetic ester with the formation of small amounts of water. In the following experiment any such possible errror is entirely eliminated. A solution of triphenylchlormethane in benzene, which had been standing over zinc six weeks, and was thus completely converted into triphenylmethyl, was siphoned over into the perfectly dry flask, *A* (Fig. 2). Although during the reaction 6

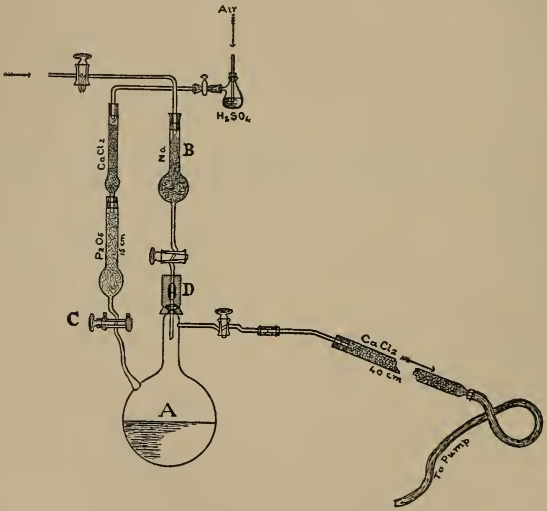


Fig. 2.

grams of zinc chloride were formed, and the benzene, therefore, must have been dry, still, in order to insure complete absence of moisture, the solution, before entering the flask *A*, was allowed to remain in contact with a large amount of metallic sodium in tube *B* for one-half hour. The stop-cocks were specially ground, stop-cock, *C*, having in addition a mercury seal. The rubber connection at *D* was entirely under mercury, and the remaining rubber connections were heavily paraffined. A slow stream of air was then allowed to enter the flask. As soon as the carbon dioxide was displaced the insoluble peroxide began to crystallize on the surface of the perfectly clear benzene solution. In a few hours the reaction was finished, and the filtrate from the peroxide gave no further precipitate on exposure to moist air. In this case, as in the two experiments with acetic ester, the oxidation was complete even when perfectly dry air was used. The quantity of the peroxide obtained in the last experiment was 5.100 grams. This, according to the theory of Norris, means an absorption of 0.1805 gram of water. No such amount of moisture could have been present.

It is of course possible that in all the experiments described, a minute trace of moisture was still present, and the oxidation was done through the catalytic influence of water. But this is a question of an entirely distinct nature and need not be discussed here. One or two molecules would suffice for the purpose of catalysis, and, as V. Meyer observed long ago,[1] we can never reach such a perfection in manipulation as to insure the absence of such minute traces of water.

The peroxide is therefore formed by the action of oxygen alone upon the unsaturated hydrocarbon. If the constitution of the peroxide is that which I have ascribed to it,

$$(C_6H_5)_3C{-}O{-}O{-}C(C_6H_5)_3,$$

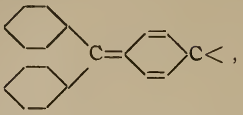
then the unsaturated hydrocarbon cannot be $(C_6H_5)_2C : C_6H_4$.

III. Is the Unsaturated Hydrocarbon Colored?

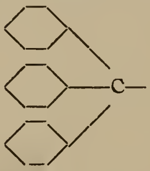
Should it be proved at some future time that the action of metals upon triphenylchlormethane results, after all, in the elimination of hydrochloric acid, the behavior of the hydrocarbon will best be explained by the constitution,

---

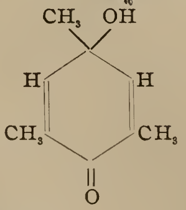
[1] Ber. d. chem. Ges., **23**, 395.

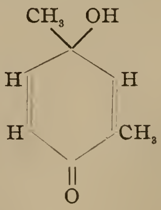


which is a modified form of Nef's[1] hypothesis, that of $\underset{\downarrow}{C_6H_4}—\underset{\downarrow}{C} = (C_6H_5)_2$, and not, as Norris assumes, by one in which the methane carbon atom is linked to 2 carbon atoms in a single benzene ring. The first formula would explain the extreme unsaturation of the hydrocarbon, while that of Norris implies a structure containing a tri-, tetra-, or pentamethylene ring, and the compound, therefore, should be fairly stable. But, for the present at least, we must assume that the metals remove only the halogen from triphenylchlormethane, and the resulting body must have, it seems to me, the constitution



The modified formula of Nef implies a half-quinoid structure. Compounds of such a constitution need not, however, be colored, as is shown by the recent work of Bamberger[2] on quinols. Thus mesitylquinol and dimethylquinol





are colorless.

---

[1] Ann. Chem. (Liebig), 309, 166.

[2] Ber. d. chem. Ges., 33, 3600.

[3] *Ibid.*, 33, 3637.

[4] *Ibid.*, 33, 3647.

It is nevertheless important to determine definitely whether the hydrocarbon under consideration is colored or not. Many attempts were made for that purpose, especially since the publication of the paper by H. Kauffmann,[1] who ascribes to triphenylmethane a tendency towards the quinoid structure on physical grounds. By precipitating the hydrocarbon from a benzene solution by means of absolute ether it is possible to obtain crystals of only very pale-yellow color, which on standing become darker. It need not necessarily follow from the fact that the solutions are always yellow that the pure substance itself must be colored. The color of the solution may be due either to an intermediate oxidation product of the hydrocarbon or to some accompanying impurities. By dissolving in carbon disulphide the pale-yellow crystals formed with acetic ester as a solvent, and precipitating with acetic ether, I obtained the crystals perfectly colorless. It is my intention to test this result in several different ways before it can be considered as settled.

In conclusion, I wish to state that this work will be continued, and I ask again that the field may be reserved for myself for a while longer.

CHEMICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
February 28, 1901.

REPORTS.

International Atomic Weights (II).

It is of interest to note in connection with the report of the Committee of the German Chemical Society (which has already been reviewed in this Journal, Vol. 24, p. 377) that several other countries and organizations have decided in favor of adopting as the standard of atomic weights the value O = 16.000. The chemists of France, who had not expressed their opinions at the time of the last report, declared themselves in favor of this standard at the Congress of Applied Chemistry, in Paris, in 1900, and the Swiss Committee has joined the movement. Fully as important is the very emphatic declaration of the Deutsche electrochemische Gesellschaft, who announce their determination to adhere to O = 16, because of its relation to the electrochemical equivalent, whatever the pure chemists may decide to do.[2]

---

[1] Ber. d. chem. Ges., **33**, 1725.

[2] Ztschr. anorg. Chem., **25**, 341 (1900).

It is both singular and unfortunate that the most serious opposition to the movement is to be found in Germany itself, the birthplace of the desire for uniformity. The report comes that Wislicenus, Winkler, Erdmann, and the other well-known adherents of $O = 15.88$ (or $H = 1$)[2] have found a large following among the teachers in Gymnasia and Realschulen. While undoubtedly the teacher's side of the question is an important one, it is only one side of a matter with manifold relationships. Of course, if in the new standard $O = 15.88$ really presents great advantages to the teacher (a supposition which may well be doubtful), and if in consequence all men who are primarily teachers should vote for this new standard, the numerical majority would be overwhelming in its favor because of the predominance of teachers. Nevertheless this overwhelming majority would represent only a single point of view, and the importance of this single point of view in relation to the more purely scientific aspects of the matter is a question worthy of debate.

When the letters asked for by the German Committee have been published, we shall have further light upon the subject, but for the present the published majority is very strongly in favor of $O = 16.000$. Whatever may be the outcome, one hopes that the whole world may accept it, for uniformity and stability are advantages which will in time be seen to outweigh all other arguments on either side of the question.

January 5, 1901. T. W. R.

The Higher Superoxides of Hydrogen.

Since the note on this subject appeared in this JOURNAL, two criticisms of Bach's work and his answer to them have appeared. Armstrong[2] claimed that Bach had failed to take into account the existence of persulphuric acid in his mixture of hydrogen peroxide and sulphuric acid, which would account for the abnormal evolution of oxygen when such a mixture is titrated with potassium permanganate, and that further, the hydrogen peroxide which he obtained from the peroxides of the metals, probably also contained persulphuric acid. Again, Bach regarded the fact that other dehydrating agents besides sulphuric acid, when mixed with hydrogen peroxide, produce effects similar to those obtained in using Caro's reagent, as evidence that hydrogen peroxide is converted into

---

[1] The adherents of this standard are inclined to consider themselves conservatives, and maintain that they are preserving the old order of things. On the other hand I am inclined to call any standard of measurement a new one which changes the numerical magnitude of all the values measured by the standard.

[2] Proc. Chem. Soc., 1900, 134.

hydrogen tetroxide by dehydration. Armstrong pointed out that the effects produced by Caro's reagent are merely such as would be expected from the action of hydrogen peroxide in the presence of a strong dehydrating and hydrolyzing agent, so that it is unnecessary to assume the existence of any new compound to explain them.

Berthelot[1] found that when he treated a solution of hydrogen peroxide and sulphuric acid with potassium permanganate in sulphuric acid, both solutions being cooled to —12° C., until there was no further decoloration, there was no effervescence. When the mixture was removed from the refrigerant and shaken, there was a rapid evolution of gas. He explained these phenomena by saying that hydrogen trioxide, H_2O_3, was formed which was stable only at low temperatures and decomposed with the evolution of oxygen as soon as it was removed from the refrigerant.

Baeyer and Villiger[2] repeated the experiment of Berthelot and found that the phenomenon observed was merely one of supersaturation. If hydrogen trioxide was formed in Berthelot's mixture, then it should not be decomposed by shaking at the temperature, —12°, at which it was formed. However, when Baeyer and Villiger repeated the experiment, they found that when the solution was shaken at —12° the theoretical amount of oxygen was evolved, and was the same in quantity as when the potassium permanganate and hydrogen peroxide reacted at +15°. The only difference between the actions at the two temperatures was that at the lower temperature the oxygen was evolved only half as rapidly as at the higher. In both cases the same, theoretically correct amounts of oxygen were liberated. On the strength of this experiment the authors claim that the experimental evidence in favor of the existence of hydrogen trioxide is of no value.

Bach[3] recently published results of the action of potassium permanganate on Caro's acid, which led him to think that the latter contained hydrogen tetroxide. Baeyer and Villiger[4] have also repeated his experiments, and while they admit his observations to be correct, they do not accept his interpretation of them.

Bach found that when a mixture of hydrogen peroxide and sulphuric acid in such proportions as to contain Caro's acid and an excess of the peroxide, was treated with potassium permanganate, the amount of oxygen evolved was more than twice as much as would be normally evolved from the permanganate alone.

---

[1] Ann. chim. phys., [5], **21**, 176.

[2] Ber. d. chem. Ges., **33**, 2488.

[3] *Ibid.*, **33**, 1506.

[4] *Loc. cit.*

As he had worked with a mixture of hydrogen peroxide and Caro's acid, Baeyer and Villiger first tried the action of potassium permanganate on Caro's acid alone, which was prepared by mixing together potassium persulphate and concentrated sulphuric acid, pouring the mixture on ice, and diluting. They showed that this acid was free from hydrogen peroxide. It was shown by them that no reaction takes place between potassium permanganate and pure Caro's acid in acid solution. However, they did confirm Bach's results in regard to the evolution of an amount of oxygen greater than that called for by the theory when a mixture of hydrogen peroxide and Caro's acid is treated with potassium permanganate, but they explain this abnormality in a different way.

They attribute it to a catalytic decomposition of Caro's acid, due to the presence of manganous sulphate. They claim that as soon as a small amount of potassium permanganate is reduced, the manganous sulphate thus formed is oxidized to manganic sulphate, and that this then acts catalytically on Caro's acid, causing its decomposition and liberating oxygen. Baeyer and Villiger also found that an excess of manganous sulphate does not act as well as a small amount in decomposing Caro's acid, hence in the reaction between potassium permanganate, hydrogen peroxide, and Caro's acid, a maximum is reached in the decomposition of Caro's acid, as soon as manganous sulphate is formed in too large a quantity. These results then appear to destroy the experimental foundation for the existence of hydrogen tetroxide.

In concluding their paper, Baeyer and Villiger discuss the three views of the action of potassium permanganate on hydrogen peroxide.

According to Schönbein, the permanganate and the peroxide simultaneously evolve atomic oxygen which then condenses to molecular oxygen. Hydrogen peroxide would thus appear to be an oxidizing agent, while in all its other reactions it is a reducing agent. Further, Caro's acid ought to react all the more easily with potassium permanganate, while, as a matter of fact, it does not react at all with it.

Berthelot's view is that the peroxide is first oxidized to the trioxide, which then breaks down into water and oxygen. Baeyer and Villiger have shown his views to be erroneous.

The most probable view seems to be that of Weltzien and Traube, according to which the permanganate oxidizes the hydrogen of the peroxide to water, while the oxygen is set free. Thus all of the oxygen liberated comes from the peroxide. The fact that Caro's acid does not react with potassium permanganate does not stand in opposition to this view, since in other cases easily oxidizable hydrogen is rendered more difficultly oxidizable by union with a negative group, as is seen on comparing the behavior of phosphine, hypophosphorous acid, and phosphorous acid.

In answering Armstrong's criticisms that his solutions of normal sulphuric acid and hydrogen peroxide might have contained some persulphuric acid, which then caused the excess of oxygen to be evolved, Bach[1] calls attention to the fact that in his check experiments with potassium permanganate and hydrogen peroxide diluted with normal sulphuric acid, amounts of oxygen were always evolved closely approximating the theoretical amounts, but never exceeding them. Thus Armstrong's criticism seems to be met.

With reference to the criticisms of Armstrong as well as of Baeyer and Villiger of his work with Caro's acid, Bach lays stress on the fact that he was working with a concentrated Caro's acid, while Baeyer and Villiger always worked with a dilute acid.

Baeyer and Villiger claimed that Caro's acid would not react with potassium permanganate and that hence the decomposition of the acid must be catalytic. Bach, on the other hand, found that concentrated Caro's acid reacted very readily with strong potassium permanganate. He was able to titrate potassium permanganate, dry or in solution, in concentrated sulphuric acid with concentrated Caro's acid, and by measuring the oxygen evolved found it to be in accord with the theory. Further, he showed that concentrated Caro's acid was not decomposed by manganous sulphate at ordinary temperatures, nor by the solution after titration with potassium permanganate. Hence, he concludes that the excess of oxygen which he obtained in his first experiments comes from a higher persulphuric acid $(HO_3S.O.O.SO_3H)_3$, which contains an active oxygen atom and which yields twice the theoretical amount of oxygen when titrated with permanganate. When working with the compound $H_2SO_4 + H_2O$ partial hydrolysis takes place with the splitting off of sulphuric acid, H_2SO_4, and the formation of tripersulphuric acid, $(HO_3S.O.OH)_3$, the concentrated Caro's acid, which, upon further dilution, breaks down into simple molecules of monopersulphuric acid, $HO_3S.O.OH$, and this reacts only slowly with potassium permanganate and is susceptible to catalytic decomposition. That concentrated Caro's acid contains three oxygen atoms united to one another follows from an observation of Bamberger that dilute Caro's acid neutralized with potassium carbonate and heated with a catalyser yields ozone.

---

[1] Ber. d. chem. Ges., 33, 3111.

Bach thinks that his views on Caro's acid are as fully justified as are those of Baeyer and Villiger, only his apply to the concentrated acid, while theirs apply to the dilute.

C. E. C.

A Recent View of Atomic Structure.

Recent observations[1] on electrically charged gases have necessitated a change of views in regard to the ultimate divisibility of matter. These new conceptions apply as yet only to gases, and they are based wholly upon physical studies. The subject is, however, of great interest to the chemist, as the atom is his unit, and anything that goes to show that this is capable of subdivision, strikes at the foundations of chemistry. Much of the work which has led to these interesting results has been done by Prof. J. J. Thomson, who has devised many experiments to clear up doubtful points. Some experiments have been made which show that the molecules of a gas and the particles of the same gas which carry the electrical charges, when a current is passed through it, are not of the same size or nature. It has been shown that there is a striking analogy between a dilute solution of an electrolyte and a gas exposed to the Röntgen rays, and that these rays have the power to dissociate the gas into its oppositely charged ions. Such a dissociated gas is a conductor and will rapidly discharge a charged metal plate, while a gas under ordinary conditions and protected from all influences which can cause dissociation, can come in contact with an insulated charged metal plate without removing any of its charge, although myriads of its molecules come in contact with the plate, whose unit surface contains only such a charge as could be carried thousands of millions times by a cubic centimeter of hydrogen.

That the electrified particle, under ordinary conditions of pressure, is more complex than the molecule is indicated by a result obtained by Mr. Townsend, who found that electrified hydrogen does not diffuse through a porous cup as rapidly as the same gas in the ordinary conditions—a fact probably due to the aggregation of the particles about one as a nucleus. Another point in favor of the view that the ordinary gas differs from the charged one is that, whenever a gas becomes a conductor when heated, it can be shown, by purely chemical means, that chemical decomposition has been caused by the heat and that the conductivity is not due to the increase in temperature. Such an action occurs when the gas is split up into atoms by heat; but when it is broken up into simpler molecules and not into atoms it does not show the conductivity.

---

[1] The Discharge of Electricity through Gases, J. J. Thomson, 1898. Les Rayons Cathodiquis, P. Villard, 1900. Phil. Mag., **44**, 293; **46**, 528; **48**, 547. Phil. Trans., **193**, 129 (1896).

The figures given for the absolute size of the molecules of gases are so uncertain that no correct idea of the absolute charge can be gained in this way; but a method has been devised which will probably give a more correct value. When an electrified gas is admitted into a vessel containing water vapor, even if the gas in the vessel is not saturated, a fog is formed, and from a knowledge of the number of water particles, which can be determined, and the total charge, the atomic charge can be determined. That the current is carried through the gas by the movement of oppositely charged particles, was shown in the following way: Two tubes containing electrodes, placed about 2 mm. from the ends of the tubes, were introduced into a vessel containing water, and bent in such a way as to bring the ends of the two tubes about 2 mm. apart. The other ends of the tubes were inserted under test-tubes to collect the gas formed. When the air had been driven out of the vessel and the water heated until it was filled with the vapor, a current was passed and the gases formed were driven up the tubes by the steam. When the gas collected was exploded to remove the hydrogen and oxygen, which were present in the proportions to form water and which had been formed along the spark, there remained in the tubes an excess of gas which in one tube was mostly hydrogen and in the other mostly oxygen, and in amount these bore a similar relation to the amount of electricity which had been passed through the vapor. We thus see that the passage of the current through the gas is due to the oppositely charged ions, and it has been shown that the gas can be rendered a conductor by the action of light, Röntgen rays and heat which serve as dissociating agents.

A study of the phenomena occurring when the current is passed through a tube exhausted to a fraction of a millimeter showed that under the conditions of the experiment there is a formation of rays with properties different from any before observed. From the fact that these appeared to start from the cathode they were called cathode rays and were supposed by Goldstein and later by Wiedemann, Hertz, and Lénard to be due to waves in the ether. This so-called "ether theory" was accepted by many as it sufficed to explain the phosphorescence, and mechanical and heating effects; but the peculiar action of the rays in a magnetic field could not be explained unless it was regarded as *sui generis*. In order to explain this and other facts Crookes suggested that the rays consist of minute particles of matter charged with negative electricity and moving at a high velocity. For a time both the "ether theory" and the "corpuscular theory" had their supporters; but at the present time the latter is the one generally accepted. The advocates of the former theory would not grant the possibility of the particles penetrating solid matter and passing through unchanged, while the opponents pointed out that no case was known in which vibrations of the ether behaved as these rays did in a magnetic field. In high vacuo the passage of the rays can be traced by the phosphorescence inside the tube and on the glass.

The rays render many substances, as the diamond, ruby, calcium fluoride, barium platinocyanide, etc., phosphorescent, and such bodies then emit the Röntgen rays. The mechanical effects of the cathode rays can be shown by their action upon small vanes mounted in the tube on an axis so that the rays strike the tops of the vanes as they are revolved by their action. The heating effect of these rays is so great that a piece of platinum iridium mounted at the focus of the rays can be heated to the fusing-point, and the surface of a diamond can be converted into graphite, indicating a temperature of at least 3600°. These effects can be explained as due to radiant energy comparable to light or to the shock of material particles moving with great velocity. These rays are charged with negative electricity, and it is impossible to change the path of the rays without changing the course of the negative electrification. The rays are deflected by an electrostatic field, and passage between two plates whose potential difference is as little as 2 volts will produce this result. In a given magnetic field, with a given potential difference between the terminals, the magnetic deflection is the same in all gases, the similarity extending to the slight details. The phenomena manifested by these can be satisfactorily explained, according to Thomson, by considering them to be particles of matter carrying a negative charge. Properties of the rays, based on this conception, can be predicted, and they have been found upon investigation to agree with those predicted.

In order to get some idea of the probable size of the particles, Thomson studied the action of the rays on a thermoelectric junction and, from the observations made here and a knowledge of certain necessary data, he was able to determine the value of m/e, where m is the mass and e the charge. As the value of m/e as thus determined was found to be 1/500 of that of hydrogen, which is 10^{-4}, in the case of the ordinary electrolysis of liquids and gases, either the value of e must be much greater than that carried by an ion of an electrolyte, or the value m of the corpuscle must be very small as compared with that of the ion.

Whether the small value of m/e, which was found to be entirely independent of the nature of the gas and of the electrode, was due to e being greater or m smaller than the value of these for the ion in electrolysis was not determined until it was shown that the value of m/e for ultraviolet light and for the negative electrification produced by an incandescent carbon filament were the same as in the cathode ray, and that a direct determination of the value of e gave a value which was the same as the charge carried by the hydrogen ion in the electrolysis of solutions. As the value of e is therefore the same, the value for m, or the mass, is much smaller than the atom, being about 1/1000 that of the hydrogen atom.

Professor Thomson thinks that the passage of the current through the gas, which is at a low pressure, causes a breaking off of a part of one or more atoms, the part broken off having a unit charge of negative electricity and being very small as compared with the part left behind which takes a positive charge, and is comparable to a mass of ordinary atoms, so that the particle which escapes with the negative charge is a small part of an atom perhaps of a mass. This, with the other evidence, leads to the assumption that the atom is composed of corpuscles and holes, the latter predominating, so that in a gas at low pressure there would be little probability of these corpuscles colliding, and they can, on account of their small size and great velocity, which is about 40,000 kilometers per second, penetrate the intramolecular spaces of solid bodies, especially as the mass of these particles is only about $3/10^{-26}$ of a gram.

This corpuscle may be the fundamental quantity in terms of which all electrical processes can be explained, as its *mass* and *charge* are invariable and independent of the *method of its formation* and of the *gas* which is present in the tube.

This conception as to the presence of corpuscles in atoms might be regarded as evidence in favor of the view held by Prout and others regarding the presence of primordial atoms in all substances, but Thomson points out that this could not be due to hydrogen as Prout supposed, as all the evidence seems to show that the size of the corpuscle is very small as compared with the hydrogen atom.

When changes in the electrical charge of an atom occur, they are due to the movements of corpuscles from the atom, when the positive charge is increased, and to the atom when the negative atom is increased. The liberation of anions and cations in electrolysis of solutions consists in the passage of a corpuscle from the electrode to neutralize the positive charge and one from the ion to the electrode to neutralize the negative charge of the ion. Accordingly, the mass of the atom is not invariable, and when hydrochloric acid is electrolyzed we have ions of hydrogen in which the mass of the atom is less than half the mass of the hydrogen molecule, H_2, and that of chlorine greater than half that of the chlorine molecule, Cl_2. Thomson thinks that not more than one corpuscle is broken off from any one atom, but that methods may be discovered which will enable us to set all the corpuscles free.

Although these particles cause a marked chemical action in a number of cases, it is impossible to isolate and collect them as the amount formed is so slight. Thomson has calculated that with the coil which he used for the experiments, running night and day for a year, the amount produced would be only *one three-millionth of a gram.* Goldstein has shown that the haloid salts of the alkaline metals are colored by the cathode rays as are those of silver, lead, and mercury. This change in color can be observed for several months if the material is kept in the dark, but exposure to light, and especially heating, restores the color. In the former cases it has been shown that a liberation of halogen takes place and that the absorption spectra of these substances are identical with the spectra of the halides which have been exposed to the vapors of the metal. The salts thus reduced show great photographic activity, and in some cases substances that have been exposed to the rays become luminous at a point far below that at which they ordinarily show the same properties. The rays, in general, act as reducing agents, as can readily be shown by exposing a silicate, rich in lead silicate, to the rays, when rapid reduction, even in the interior of the crystal, takes place. When copper silicate, which is clear and colorless, is exposed to the rays there is a formation of a red cuprous compound. Glass often becomes dark when exposed to the rays as it does when exposed to the action of the reducing flame. J. E. G.

Combustible Gases in the Atmosphere.

In a recent number (January, 1901) of the Annales de Chimie et de Physique there is a summary of the results obtained by Gautier during an investigation which has been in progress for a number of years upon the combustible gases of the air and the presence of hydrogen as a constituent of the atmosphere. The careful attention to details and the thoroughness of the work as well as the methods, which have been used to overcome obstacles, especially impresses one who studies these results. Before this work could be taken up it was necessary to test the accuracy of the methods which had been suggested for the detection and determination of the gases to be studied, and in some cases to determine the exact conditions which would give the correct results. In order to determine with great accuracy the amount of combustible gases in the air, by converting them into carbon dioxide and water, it was first necessary to remove all the acid gases and moisture, a result which is not as simple as it appears *a priori*.

It was found impossible entirely to remove the carbon dioxide from a gas in which it was present in amounts less than $\frac{1}{100000}$ of the total gas, by passing it through a solution of potassium hydroxide; but if this was then passed through a tube containing crystallized barium hydroxide the last trace was easily removed. In order to remove the moisture he found it necessary to pass it through a small quantity of pure sulphuric acid, which had been boiled, and then over phosphorus pentoxide which had been saturated with oxygen at 260°. A careful examination showed that no appreciable amount of the sulphuric acid vapor was carried off by the gas under the conditions used.

A number of the methods which have been suggested for the determination of carbon monoxide were found to be inaccurate and not sensitive if the carbon monoxide was present only in small quantities; but one method was worked out which makes it possible to estimate carbon monoxide rapidly and accurately, when mixed with 10,000 to 20,000 times its volume of air. The reaction which takes place and which is complete at 65° to 75°, whatever the dilution of the gas may be, is represented by the following equation:

$$5CO + I_2O_5 = 5CO_2 + I_2.$$

If it were practicable to determine the amount of carbon dioxide formed, 1 part of the monoxide to 100,000–300,000 of air could be detected by this reaction. It was also shown that this great accuracy could be secured even in the presence of other gases present in the atmosphere, as these gases do not act on the pentoxide of iodine at the temperature of the reaction.

By the methods which have been described Gautier was able to remove the acid gases, as well as water and carbon monoxide, and was then in a position to study the methods that could be used for the detection and determination of the hydrocarbons and hydrogen in the air.

When hydrogen at a dilution of $\frac{20}{1000000}$,—about that in which it is present in air,—is passed over a layer of copper oxide about 70 cm. long, at the rate of 2 to 3 liters per hour, it is completely oxidized; but if the layer of oxide is only 30 cm. long, only about 70 per cent of the hydrogen is oxidized. When a mixture of hydrogen and hydrocarbons is passed over the copper oxide, the hydrogen is oxidized first and the hydrocarbons are changed into hydrocarbons which are more difficult to oxidize. This necessitates the use of a layer of the oxide 80 cm. long to oxidize the gases completely. Experiments with mixtures of copper oxide with other oxides and platinum sponge gave no better results. It was also found that after long use the oxide will partly oxidize the hydrogen, but will not act at all on the hydrocarbons. Special forms of absorption apparatus and a furnace, in which the temperature could be carefully regulated, were used in this work.

By a comparison of the results obtained with the air of the city, of the country, of high snow-covered mountains where great privations were suffered in order that the air might not be contaminated by the products of combustion from a fire, and of the sea, it was shown that hydrogen is present in the atmosphere to the extent of about $\frac{2}{10000}$ of its volume, and that the air of cities and the country contain hydrocarbons which are probably derived from combustion processes, fermentation processes, and from the earth. The results indicate that, while methane occurs in considerable quantity, other hydrocarbons are also present, and the following table gives the number of cubic centimeters of the combustible gases contained in 100 liters of city air. These quantities are, however, subject to variations due to local conditions:

Free hydrogen	19.4
Methane	12.1
Benzene	1.7
Carbon monoxide	0.2

While the amounts of oxygen, carbon dioxide, and nitrogen are about constant, owing to the changes taking place in animal and plant life, the amount of hydrogen and methane seems to be steadily increasing. He points out that these gases are present in volcanic gases and that, while much of it is burned under ordinary conditions, when the action takes place under the sea the gases are cooled and escape unchanged. Volcanic action has been going on for ages, and all solid rocks show evidence of such action, as they contain the gaseous products in cavities of the rocks. When granite is pulverized and heated, or sometimes treated with water and acid, a considerable volume of gas is obtained which consists of carbon dioxide, hydrogen sulphide, methane, hydrogen, and several others. Even water alone will set free a large amount of gas if the temperature is raised to 280° to 300° C. Gautier considers that, in the cooling of the constituents of the earth, compounds were formed which are unstable, and that, if we could investigate the composition of the interior of the earth, we should find sulphides, nitrides, carbides, fluorides, phosphides, etc., which by decomposition with water would form the gases actually observed in volcanic gases.

There are several methods by which the origin of the hydrogen can be explained: (*a*) By the decomposition, at red heat, of water by ferrous salts; (*b*) by the decomposition, by heat, of the hydrocarbons formed from carbides; and (*c*) in small quantity, by the decomposition of such a compound as iron nitride; thus: $N_2Fe_6 + 6H_2O = 2NH_3 + 6FeO + 6H$, a reaction which has been observed when a crystalline nitride of iron found in Etna lava was treated with water.

These and other substances are present in small quantities in rocks and are decomposed by the water which penetrates the rocks with the formation of methane, petroleum, hydrogen, etc. These gases slowly pass upward and, while the acid and active gases probably react with some substances with which they come in contact, the inactive ones finally escape from the surface. Although hydrogen is constantly being set free, an explanation of the small quantity present in the atmosphere may perhaps be due to the same cause that has been assigned by Johnstone Stoney to explain the absence of helium in quantity, its escape into interplanetary space on account of its great velocity. J. E. G.

REVIEWS.

AIR, WATER, AND FOOD FROM A SANITARY STANDPOINT. By ELLEN H. RICHARDS AND ALPHEUS G. WOODMAN, Instructors in Sanitary Chemistry, Massachusetts Institute of Technology. First edition. New York: John Wiley & Sons. 1900.

Designed as a manual for college study, this book fulfils its purpose admirably. Thirty-two pages are given to air, its impurities, ventilation, and analytical methods. Eighty pages are given to water, 100 pages to food. The better analytical methods are clearly described. Excellent tables of food values, of analyses of normal and polluted waters, etc., and a list of the more important books on the subject, enhance the value of this manual.

A quotation will show the interesting way in which Mrs. Richards writes: "The sophists were educated and intelligent men, and persuaded the people by specious reasoning. The modern 'pure food' manufacturer is a sophist who, with great skill and by the aid of the well-paid experts, persuades the general public that he is their benefactor in that his chemists have penetrated nature's secrets, hidden from the ordinary man, and therefore that he is able to offer them long life and prosperity at so many cents to the pound.....To adulterate the coin of the realm or the liquor of the bar with a baser metal or an imitation whiskey is a heinous offense.....But the 'wretched sophistry' which obscures the nature of things on a package of prepared food misleads more persons and inflicts more injury on the community than the other, and yet goes unrebuked.....This craving for something new to stimulate a jaded appetite already spoiled by endless variety and bad combinations has led to the manufacture of a cereal preparation for nearly every day in the year.....

"The excessive fear of indigestible food which prevails among the wealthier classes may lead to universal debility of the intestinal muscular walls.[1] This fear and the lack of exercise is working mischief especially among students."

If space permitted, the reviewer would give further quotations to show the authors keen common sense. E. R.

EVOLUTION OF THE THERMOMETER: 1592–1743. BY HENRY CARRINGTON BOLTON. Easton, Pa.: The Chemical Publishing Co. 1900. 98 pp. Price, $1.00.

This interesting little book contains much curious information. Its author is careful to call attention to the many steps that had to be taken before the crude open air-thermometer or, rather, thermoscope, of the age of Galileo—an instrument with no scale or with an entirely arbitrary one—should be developed into the closed mercury or alcohol thermometer of Celsius, provided with a scale based upon two clearly defined "fixed points." Many distinguished men of science participated in bringing about this progress; in addition to the names of Fahrenheit, Rèaumur, and Celsius, so generally associated with the development of thermometry, it is interesting to hear of the contributions made by Galileo, the Florentine Academy, Boyle and Newton—to mention but a few.

The principal steps in this development were (1) the adoption of a scale of degrees for making comparisons of temperatures; (2) the substitution of a closed thermometer for one subject to variations on account of changes in atmospheric pressure; (3) the adoption of alcohol and of mercury as the substances whose expansion and contraction serve as a measure of changes of temperature; (4) the realization of the advantages of a scale having clearly defined "fixed points;" (5) the choice of the boiling-point of water at standard pressure and of the melting point of ice as the fixed points of the scale.

The temptation to quote at some length is a great one, but space is wanting. It is to be hoped that many will avail themselves of the benefits offered by Dr. Bolton's careful piece of historical research. W. W. R.

---

[1] Bunge: "Physiological Chemistry."

VOL. XXV. MAY, 1901. No. 5.

AMERICAN

CHEMICAL JOURNAL

CONTRIBUTION TO THE STUDY OF AQUEOUS SOLUTIONS OF DOUBLE SALTS.

IV.—IODIDES, CYANIDES, NITRATES, AND SULPHATES.[1]

BY HARRY C. JONES AND B. PALMER CALDWELL.

The large number of investigations which have had to do with the problem of the condition of double salts in solution have been discussed briefly by Jones and Mackay.[2] It remains to consider here the work which has been done since their paper appeared.

Double salts in general have been divided into two classes by Ostwald,[3] who distinguishes between what he terms "complex salts" and "double salts." The former include those molecular complexes which are capable of existing as such in aqueous solution—not undergoing decomposition into their constituent salts. These dissociate into a cation consisting of the more positive metal, and an anion consisting of the acid complex. For example, potassium ferrocyanide is dissociated in water into :

$$\overset{+}{K} + \overset{+}{K} + \overset{+}{K} + \overset{+}{K} + Fe(\overset{\overline{\equiv}}{CN})_6.$$

---

[1] From the dissertation of B. P. Caldwell, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, January, 1901.

[2] This JOURNAL, 19, 83.

[3] Ztschr. phys. Chem., 3, 599.

"Double salts" are supposed to break down at once in water into their constituents, and are formed only at the instant when the double salt crystallizes out from the solution.

There are, however, all gradations between "complex" and "double salts." Many "double salts," although largely decomposed by water into their constituents, are still capable of existing to some extent in concentrated solutions.

A special study has been made in this laboratory of the conductivity of double salts, which would not ordinarily be classed among the complex salts. Jones and Mackay[1] studied certain alums and found that the difference between the conductivity of the alums and the sum of the conductivities of the constituent salts was greater than that which exists between the conductivity of mixtures of salts not capable of forming double salts, and the sum of their separate conductivities. They concluded that the alums studied are to be classed as true double salts, even while in solution. At very great dilution, however, no distinction could be drawn between their behavior and that of a mixture of the constituents.

Somewhat later Jones and Ota[2] extended the work to certain double chlorides and obtained, in general, the same results. It was evident, however, that the solution assumes the condition of a mixture of the constituent salts at much smaller dilution, that is, the complex ion breaks down into simpler ones much more easily under the influence of increasing dilution than in the double sulphates. Jones and Knight[3] continued the work and investigated the behavior of certain other double chlorides and double bromides. As the work here described is an extension of the above to certain double sulphates (not alums), iodides, cyanides, and nitrates, and as the same method of work was adopted, it need not be more fully discussed here.

Reasoning from Arrhenius' theory of isohydric solutions MacGregor[4] has deduced certain methods for calculating the conductivity (and other properties of the ions), of mixtures of electrolytes which do not act upon one another chemically. These were based upon the quantities of the single constituents present in a given volume of the solution, the amounts of their dissociation, and their molecular conductivities at infinite dilution.

---

[1] This JOURNAL, **19**, 83.

[2] *Ibid.*, **22**, 5.

[3] *Ibid.*, **22**, 110.

[4] Phil. Mag., [5], **41**, 276 (1896); Trans. N. S. Inst. Sci., **9**, 101; Trans. Roy. Soc. Can., (2) **2**, sec. 3, 65.

If v is the volume of a solution which contains n_1, n_2, n_3, $\ldots$, etc., gram equivalents of the respective electrolytes present; if a_1, a_2, a_3, $\ldots$, etc., are their respective coefficients of dissociation or ionization, and if μ_{a_1}, μ_{a_2}, μ_{a_3}, $\ldots$ etc., are their respective specific conductivities per gram-equivalent at infinite dilution, then, according to the above theory, the specific conductivity of the solution is equal to:

$$\frac{1}{v}\left(a_1 n_1 \mu_{a_1} + a_2 n_2 \mu_{a_2} + a_3 n_3 \mu_{a_3} + \ldots \text{ etc.}\right).$$

He then deduces four equations which, if graphically employed, enable one to calculate the conductivity of mixtures of electrolytes to a high degree of accuracy in dilute solutions. In a mixture of electrolytes each may be considered as occupying its own distinct portion of the solution. If we denote the electrolytes by 1 and 2, the concentrations (in gram-equivalents per liter) of the solution with respect to them by n_1 and n_2, respectively, their ionization coefficients by a_1 and a_2, and their regional dilutions (in liters per gram-equivalents) by v_1 and v_2, respectively, then, when the solutions are in equilibrium with respect to each other,

$$\frac{a_1}{v_1} = \frac{a_2}{v_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1),$$

that is, the numbers of the free gram-ions of the electrolytes per unit volume of their respective regions are equal;

$$n_1 v_1 + n_2 v_2 = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2),$$

that is, the volume of the solution is equal to the sum of the volumes of the regions of the respective electrolytes;

$$\frac{a_1}{v_1} = f_1(v_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3),$$

$$\frac{a_2}{v_2} = f_2(v_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4),$$

that is, the regional ionic concentrations are functions of the respective regional dilutions.

By means of curves these relations are worked out more easily than by pure mathematics, and the estimation of the conductivity of mixtures at different dilutions can be accurately made. In testing MacGregor's graphical method the work of his students[1] has shown that in dilute solutions it holds accurately, but that in more concentrated solutions, where the μ_a of the constituent salts cannot be considered the same (due to the presence of a large quantity of another salt) as when water alone is the solvent, discrepancies arise.

The large amount of work which has been done thus far on the condition of double salts in solution would seem to justify the following conclusions :

Ostwald's distinction between "complex" and "double salts" holds fairly well in very dilute solutions. In such solutions "double salts" break down completely into their constituents and these dissociate in the usual manner. "Complex salts," on the other hand, do not completely break down into their constituents, even at very great dilutions, although they show a marked tendency to decompose as the dilution of the solution is increased. Those salts which, in dilute solution, have different properties from those of the constituents, give, on electrolysis, a complex anion. Thus, the compound K_2PtCl_6, when electrolyzed, yields the ions $\overset{+}{K} + \overset{+}{K} + \overset{=}{PtCl_6}$. "Double salts," in dilute solution, are completely broken down into their constituents, and, therefore, do not yield any such complex anion when subjected to electrolysis.

It has been pointed out that the distinction between "complex salts" and "double salts" does not hold at all in concentrated solutions. Many so-called double salts exist to a very considerable extent in concentrated solution, as has been shown especially by the work which has been done in this laboratory.

The present investigation was undertaken with the desire of obtaining further knowledge with respect to certain groups of substances which had already been studied to some extent, and also to acquire information concerning classes of substances about which little or nothing was known. Our work includes a number of double sulphates which are not alums, certain double nitrates and iodides, and a double cyanide. The work consists in comparing the molecular conductivities of the double salts with the sum of the conductivities of their constituents under the same conditions of concentration. Some freezing-point work was also done.

---

[1] McIntosh : Trans. N. S. Inst. Sci., **9**, 120 (1895-'96) ; Phil. Mag., (5), **4**, 510 (1896); Archibald : Trans. N. S. Inst. Sci., **9**, 291, 307, 335 ; Trans. Roy. Soc., Can., (2), **3**, sec. III., 69 (1897-'98). McKay : Trans. N. S. Inst. Sci., **9**, 321 (1897-'98).

METHOD OF WORK.

The Kohlrausch method of measuring conductivity was employed, a "manganin" wire being used upon the bridge. The induction coil[1] which we used gave such unusual satisfaction that it calls for special comment. By a system of very rigid, thick, steel bars, carrying the make and break spring, an exceptionally high pitch was obtained. The whole was encased in a box, the connections leading to binding-posts on the outside. The adjusting screw was controlled from the exterior. The coil was so noiseless that it could easily have been used on the same desk with the bridge. For convenience it was placed some distance from the bridge.

The resistance coils used were accurate to $\frac{1}{25}$ of 1 per cent.

Two Arrhenius cells were employed in measuring the resistances. The one, with electrodes very wide apart, was used with concentrated solutions, the other with electrodes quite close together, was employed for studying the dilute solutions. The object in using two cells was to be able to throw into the box a considerable resistance for all solutions, and at the same time never be compelled to use such a high resistance that a sharp minimum could not be obtained. The cells were frequently restandardized with a N/50 solution of potassium chloride, and the standardizations were checked by determining for every substance the conductivity of some solution in both cells. All the measuring apparatus used was calibrated by the method of Morse and Blalock.[2]

The double salts were prepared by bringing the constituent salts together in the proper proportions, dissolving the whole, and evaporating to crystallization. The crystals were freed as completely as possible from the mother-liquor by means of drying paper, and, in every case, analyzed.

---

[1] Made especially to order by M. E. Leeds & Co., Philadelphia.

[2] This JOURNAL, 16, 479.

The single constituents and double salts were dissolved in pure water, and mother-solutions of convenient strength were prepared and analyzed. From these, suitable dilutions were made. Two methods of diluting were employed. In some cases 50 cc. of the solution were measured into the conductivity cell, and after its conductivity had been determined, 25 cc. were withdrawn by means of a pipette and the same amount of water added in cases where it was wished to double the volume of the solution. In this way dilutions were made in the cell from a solution of volume 1 to volume 2, to volume 4, to volume 8, to volume 20. A solution of volume 20 was then made from the original solution directly in a measuring flask, and its conductivity compared with that of the solution made by successive dilutions in the cell. Very small differences were noted, and the proportional corrections[1] were applied to the solutions previously made. This latter solution was then diluted in the cell three or four times, and the conductivity of the last solution compared with one of the same concentration made directly from the original mother-solution.

The other method of diluting was very simple. It consisted in making each dilution directly from the mother-solution. For example, from a solution of volume 1, solutions of volumes 2, 4, 8, 20, 40 would be prepared in measuring flasks. Further dilutions would then be made from the last (40) as a mother-solution.

It has been argued in favor of the first method that time is saved. We are of the opinion that not only is the second method more accurate but it does not require any more time.

All the water used in making up the solutions and washing out the apparatus was purified by distillation in the manner described by Jones and Mackay.[2] Corrections were applied to the conductivities of the dilute solutions for the conductivity of the water. The conductivity of the water was determined for each substance. The conductivity of the water ranged

[1] Kohlrausch : Wied. Ann., **26**, 184 (1885).

[2] Ztschr. phys. Chem., **22**, 237 ; This JOURNAL, **19**, 91.

from 1.1×10^{-7} to occasionally 3.0×10^{-7}. All water was preserved in vessels which had been used alone for that purpose for a number of years.

CONDUCTIVITY MEASUREMENTS.

In the work which is discussed below all the solutions were made up on the basis of the molecular weight of the substance. A solution of volume 1 contains 1 gram-molecular weight of the substance in a liter of solution. The symbol v is used to denote the number of liters of the solution which contains 1 gram-molecular weight of the substance. The symbol μ_v is used to denote the molecular conductivity of the solution at the volume v. The column marked "concentration" in the tables contains the strength of the solution in terms of 1 gram-molecule per liter as normal.

Double Iodide of Potassium and Cadmium.

The conductivity of cadmium iodide had been determined by Grotrian and Wershofen,[1] and we have interpolated from their values.

Table I.—Conductivity of Cadmium Iodide.

Cadmium iodide, CdI_2. Molec. wt., 365.70.

v.	$\mu_{v_{18°}}$.	v.	$\mu_{v_{18°}}$.
1	....	40	73.4
2	28.2	100	99.6
4	34.0	200	121.8
10	43.8	400	143.4
20	55.6	1000	171.8
		2000	183.2

The conductivity of potassium iodide had been determined by Kohlrausch,[2] and we have interpolated from his values.

Table II.—Conductivity of Potassium Iodide.

Potassium iodide, KI. Molec. wt., 166.0.

v.	$\mu_{v_{18°}}$.	$2\mu_{v_{18°}}$.	v.	$\mu_{v_{18°}}$.	$2\mu_{v_{18°}}$.
1	96.8	193.6	50	113.2	226.4
2	99.7	199.4	100	116.1	232.2
5	102.4	204.8	200	118.3	236.6
10	106.9	213.8	500	119.7	239.4
20	110.2	220.4	1000	120.3	240.6
			2000	121.2	242.4

---

[1] Wied. Ann., **18**, 177 (1883); Ztschr. phys. Chem., **5**, 481 (1890).

[2] Wied. Ann., **26**, 161 (1885).

The conductivity of the double iodide of potassium and cadmium had been determined by Grotrian and Wershofen.[1]

Table III.—Conductivity of Potassium Cadmium Iodide.

Potassium cadmium iodide, K_2CdI_4. Molec. wt., 697.70.

v.	$\mu_{v_{18°}}$.	*v*.	$\mu_{v_{18°}}$.
2	151.6	100	285.4
4	166.0	200	313.0
10	188.0	400	344.8
20	208.0	1000	378.0
40	228.8	2000	401.0
		4000	408.0

The comparison of the conductivity of the double salt with the sum of the conductivities of the constituent salts must be made so as to take into account the fact that 2 molecules of potassium iodide are present in the double salt to every one of the cadmium iodide. Twice the conductivity of the potassium iodide at one-half the dilution of the cadmium iodide is added to the conductivity of the latter, and the sum is compared with that of the double salt at the latter volume.

Table IV.—Comparison. Potassium Cadmium Iodide.

v.	$2\mu_{v_{18°}}$, KI.	*v*.	$\mu_{v_{18°}}$, CdI_2.	Sum.	$\mu_{v_{18°}}$, K_2CdI_4.	Difference.
1	193.6	2	28.2	221.8	151.6	70.2
2	199.4	4	34.0	233.4	166.0	67.4
5	204.8	10	43.8	248.6	188.0	60.6
10	213.8	20	55.6	269.4	208.0	61.4
20	220.4	40	73.4	293.8	228.8	65.8
50	226.4	100	99.6	326.0	285.4	40.6
100	232.2	200	121.8	354.0	313.0	41.0
200	236.6	400	143.4	380.0	344.8	35.2
500	239.4	1000	171.8	411.2	378.0	33.2
1000	240.6	2000	183.2	423.8	401.0	22.8
2000	242.4	4000	....	....	408.0	....

Double Iodide of Strontium and Cadmium.

This salt was prepared by dissolving together the quantities of pure cadmium iodide and strontium iodide required to make a double salt containing 1 molecule of each constituent. The double salt crystallizes readily, although it is quite soluble. It has the composition $SrCdI_4.8H_2O$.

---

[1] Wied. Ann., 18, 177; Ztschr. phys. Chem., 5, 481.

Analysis: The cadmium was precipitated from the acidified solution with hydrogen sulphide, and the strontium, after boiling off the hydrogen sulphide, was determined in the filtrate by precipitation with sodium carbonate. The cadmium sulphide was collected in a Gooch crucible and washed with chloroform and carbon bisulphide to remove any precipitated sulphur.

I. 2.2325 grams crystallized salt gave 0.3950 gram CdS and 0.3795 gram $SrCO_3$.

II. 1.9053 grams crystallized salt gave 0.3285 gram $SrCO_3$.

	Calculated for $SrI_2.CdI_2.8H_2O$.	Found. I.	II.
Cd	13.17	13.75	....
Sr	10.17	10.08	10.23

The iodine was determined by titrating the solution with N/10 silver nitrate.

	Calculated.	Found.
I	59.61	59.50

Preparation of the Solution.—The salt was weighed out approximately so as to make a normal solution when dissolved in a liter of water. A portion of the solution was diluted twenty times and titrated against the silver nitrate solution.

The original solution had a concentration 0.9944 normal and its volume was 1.0056.

Table V.—Conductivity of the Double Iodide of Strontium and Cadmium.

Strontium cadmium iodide, $SrCdI_4.8H_2O$. Molec. wt., 846.39.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25^\circ}}$.
1.0056	0.9944	846.39	91.1
2.0112	0.4972	423.19	121.9
4.0224	0.2486	211.59	144.4
10.056	0.09944	84.639	172.5
20.112	0.04972	42.319	199.9
40.224	0.02486	21.159	235.4
100.56	0.009944	8.4639	289.1
201.12	0.004972	4.2319	324.4
402.24	0.002486	2.1159	357.6
1005.6	0.000994	0.8464	393.2
2011.2	0.000497	0.4232	426.4
4022.4	0.00025	0.2116	454.5
10056.0	0.0001	0.0846	462.6

Table VI.—Conductivity of $SrCdI_4$ Calculated for Even Volumes.

$SrCdI_4$.

v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.
1	90.93	20	199.82	400	357.6
2	121.58	40	235.05	800	393.2
4	144.17	80	270.84	2000	426.4
8	162.89	200	324.39	4000	454.5

Strontium Iodide.

The salt was purified by crystallization and analyzed.

The solution for the determination of conductivity was made up and standardized by precipitating the strontium as carbonate.

The solution had a concentration of 0.7829 normal, and its volume was 1.2644.

Table VII.—Conductivity of Strontium Iodide.

Strontium iodide, SrI_2. Molec. wt. (cryst.), 449.42.

v.	Concentration.	Grams crystallized salt per liter.	μ_v.
1.2644	0.7829	351.85	150.56
2.5288	0.3914	175.92	169.29
5.0576	0.1957	87.96	181.77
12.644	0.07829	35.18	196.79
25.288	0.03914	17.59	206.04
50.576	0.01957	8.79	217.83
126.44	0.007829	3.518	229.82
252.88	0.003914	1.7592	239.12
505.76	0.001957	0.8796	245.59
1264.4	0.000729	0.3518	248.58
2528.8	0.000391	0.1759	253.89

Table VIII.—Conductivity of SrI_2 Calculated for Even Volumes.

SrI_2.

v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25}}$.
1	146.65	20	202.18	400	242.84
2	161.45	40	212.97	800	247.19
4	176.56	80	222.24	2000	251.78
8	187.59	200	235.40		

The conductivity of cadmium iodide is given above.

Table IX.—Comparison. Strontium Cadmium Iodide.

v.	$\mu_{v_{25°}}$. SrI_2.	$\mu_{v_{25°}}$. CdI_2.	Sum.	$\mu_{v_{25°}}$. $SrCdI_4$.	Difference.
1	146.65	....	....	90.93	....
2	161.45	28.2	189.6	121.58	68.0
4	176.56	34.0	210.56	144.17	66.4
8	187.59	40.6	228.2	162.89	65.3
20	202.18	55.6	257.8	199.82	58.0
40	212.97	73.4	286.4	235.05	51.4
80	222.24	91.0	313.2	270.84	42.4
200	235.40	121.8	357.2	324.29	32.9
400	242.84	143.4	386.2	357.59	28.6
800	247.19	162.4	409.6	381.2	28.4
2000	251.78	183.2	435.0	426.38	8.6

DOUBLE CYANIDE.

Double Cyanide of Potassium and Mercury.

This salt was obtained by crystallization from a solution containing the constituent salts in the proportion to form

$$2KCN.Hg(CN)_2.$$

Analysis.—The mercury was precipitated as mercuric sulphide, and was collected and weighed in a Gooch crucible. The precipitate was washed with carbon bisulphide to remove any sulphur that might have been present. The salt is very hygroscopic, and the crystals taken for analysis were dried on absorbent paper.

I. 1.3529 grams salt gave 0.8025 gram HgS.
II. 1.4593 grams salt gave 0.8641 gram HgS.

	Calculated for $2KCN.Hg(CN)_2$.	Found. I.	Found. II.
Hg	52.33	51.13	51.04

As the substances employed had been previously recrystallized a number of times, and as the crystals of double salt were well formed, and, further, since the substance used for analysis had been only dried on absorbent paper, the analysis was taken to indicate pure double salt, and it was used without further recrystallization for the purpose of the investigation.

The solution prepared for the determination of the electrical conductivity was analyzed in the same way. It was 0.8191 normal, and its volume 1.2210.

Table X.—Conductivity of the Double Cyanide of Potassium and Mercury.

Potassium mercury cyanide, $2KCN.Hg(CN)_2$. Molec. wt., 382.76.

v.	Concentration.	Grams per liter.	$\mu_{v_{25^\circ}}$.
1.221	0.8191	313.5187	155.0
2.442	0.4095	156.7593	173.1
4.884	0.2047	78.3796	186.8
12.21	0.08191	31.3518	202.0
24.42	0.04095	15.6759	211.5
48.84	0.02047	7.8379	222.0
122.1	0.008191	3.1352	234.0
244.2	0.004095	1.5676	240.0
488.4	0.002047	0.7838	244.3
1221.0	0.000819	0.3135	248.9
2442.0	0.000409	0.1567	251.2
4884.0	0.000204	0.0784	259.5
12210.0	0.000082	0.0313	258.8

Table XI.—Conductivity of $K_2Hg(CN)_4$ Calculated for Even Volumes.

$K_2Hg(CN)_4$.

v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.
2	166.5	40	217.9	800	245.6
4	181.8	80	227.1	2000	250.4
8	193.3	200	237.8		
20	208.1	400	242.8		

Mercuric Cyanide.

The solution was 0.4013 normal, and its volume was 2.4937. The conductivity of this substance is very small, so that only the most concentrated solutions gave distinct readings on the bridge.

Table XII.—Conductivity of Mercuric Cyanide.

$Hg(CN)_2$. Molec. wt., 252.38.

v.	Concentration.	Grams per liter.	$\mu_{v_{25^\circ}}$.
2.4937	0.4013	101.28	0.2775
4.9874	0.2006	50.64	0.2957
9.9748	0.1003	25.32	0.3198
24.937	0.0401	10.13	0.3787

Table XIII.—Conductivity of Mercuric Cyanide Calculated for Even Volumes.

$Hg(CN)_2$.

v.	$\mu_{v_{25°}}$.
4	0.2884
8	0.3104
20	0.3588

Potassium Cyanide.

The solution used was 1.3944 normal, and its volume 0.7171.

Table XIV.—Conductivity of Potassium Cyanide.

Potassium cyanide, KCN. Molec. wt., 65.19.

v.	Concentration.	Grams per liter.	$\mu_{v_{25°}}$.
0.7171	1.3944	90.9009	110.69
1.4342	0.6972	45.4504	119.74
2.8684	0.3486	22.7252	126.71
7.171	0.1394	9.0900	133.20
14.342	0.0697	4.5450	138.88
28.684	0.0348	2.2725	144.76
71.71	0.0139	0.9090	150.38
143.42	0.0069	0.4545	154.98
286.84	0.0035	0.2272	157.98
717.1	0.0014	0.0909	162.30

Table XV.—Conductivity of Potassium Cyanide Calculated for Even Volumes.

KCN.

v.	$\mu_{v_{25°}}$.	$2\mu_{v_{25°}}$.
1	114.26	228.52
2	122.49	244.98
4	128.41	256.82
10	135.43	270.86
20	141.20	282.40

Since the double salt has the composition $2KCN.Hg(CN)_2$, in making the comparison of its conductivity with the sum of the conductivities of the constituent salts, that of the potassium cyanide must be taken at one-half the dilution and doubled. The case is parallel to that of $2KI.CdI_2$.

Table XVI.—Comparison. Potassium Mercuric Cyanide.

v.	$2\mu_{v_{25^\circ}}$ KCN.	v.	$\mu_{v_{25^\circ}}$ $Hg(CN)_2$.	Sum.	$\mu_{v_{25^\circ}}$ $K_2Hg(CN)_4$.	Difference.
1	228.52	2	(0.25)	228.77	166.5	62.2
2	244.98	4	0.2884	245.27	181.8	63.4
4	256.82	8	0.3104	257.13	193.3	63.8
10	270.86	20	0.3588	271.22	208.1	63.1
20	282.40	40	(0.39)	282.79	217.9	64.9

The results obtained with the above double iodides and the cyanide show that these salts exist in solution undecomposed into their constituents, in part at least, up to and even beyond a dilution of 2000 liters. The "difference" in the case of the double iodide of potassium and cadmium at a volume of 1 amounts to 31 per cent of the sum of the conductivity of the constituents. In the case of the double iodide of strontium and cadmium it amounts to 35 per cent at a volume 2, and in the case of the double cyanide of potassium and mercury it amounts to 27 per cent at a volume 1.

Jones and Knight[1] found that the "difference" in the case of the double chlorides $2NaCl.ZnCl_2$ and $SrCl_2.2CdCl_2$, amounted to 35.45 per cent for concentrated solution, and that these differences persisted even at a higher dilution than 9000 liters; while in the case of mixtures of chlorides which are not capable of forming double salts, such as $KCl + NH_4Cl$ and $KCl + 2NH_4Cl$, it amounted to only 11 to 14 per cent, and entirely disappeared at about 500 liters.

No very complete information is obtainable as to the behavior of mixtures of iodides. The magnitude of their conductivity is not very different from that of the chlorides, however, and we are justified, by the well-known similarity of the behavior of halogen salts in general, in making the comparison with them. Such a comparison indicates, without doubt, that the iodides under consideration are not completely dissociated in solution. They, also, like the chlorides studied by Jones and Knight,[2] and Jones and Ota,[3] retain their compound character, somewhat, to high dilutions. We are not quite as fully justified in making the comparison of the cyanide with

[1] *Loc. cit.*

[2] *Loc. cit.*

[3] *Loc. cit.*

the chlorides, but, were we to do so, the same conclusion would be reached in regard to them as in the case of the chlorides and iodides.

A comparison with the differences shown by mixtures of bromides which do not combine to form double salts, strengthens the above conclusion. They behave exactly like the chlorides, and there is no reason for supposing that the iodides conduct themselves differently. Direct experimental proof would, however, be desirable.

Croustchoff and Packhoff[1] give some meager information in reference to the behavior of solutions of mixed halides. They find that the conductivity of the solution $\frac{1}{2}(NaBr + KI)$ actually observed is about 1 per cent smaller than that calculated from the conductivities of the constituents. The difference in the case of the solution $\frac{1}{2}(NaI + KBr)$ is given as about 3.5 per cent, while that in the case of $\frac{1}{2}(KI + NaI)$ is about 0.5 per cent.

This is the only direct experimental evidence we possess on the conductivity of mixtures of iodides, and shows clearly the existence of these double iodides in concentrated solution.

DOUBLE NITRATES.

Double Nitrate of Ammonium and Praseodymium.

It was deemed desirable to investigate the condition of double nitrates in solution. Very few double nitrates exist, however, where both constituents are soluble in water. We were fortunate in having at our disposal a fairly good quantity of praseodymium and neodymium nitrates and oxides which were in a high state of purity, having been repeatedly crystallized in the course of an investigation carried on some time ago by one of us[2] on the atomic weights of praseodymium and neodymium.

In the case of praseodymium the substances at our disposal were praseodymium nitrate and the double nitrate of praseodymium and ammonium. The method used for the purification of the materials employed, as well as their degree of purity, are recorded in the article above mentioned.

---

[1] Compt. rend., **108**, 1162.

[2] Jones : This JOURNAL, **20**, 345.

Solutions were prepared and standardized by determining the praseodymium. This was precipitated with ammonium hydroxide and the precipitate ignited to oxide in a porcelain boat. This oxide has the formula Pr_4O_7. As there is some doubt as to whether this oxide has a definite composition, the precipitate was ignited in a rapid stream of hydrogen, purified by passing through lead plumbate and silver nitrate; then dried by passing through sulphuric acid, and reduced to the well-known compound Pr_2O_3.

The loss in weight on ignition in hydrogen and the equal gain in weight on subsequent ignition in air convinced us that the oxide Pr_4O_7 does exist, and can be used in the analysis of praseodymium salts.

The concentration of the solution used was 1.2072 normal, and its volume 0.8314.

Table XVII.—Conductivity of the Double Nitrate of Ammonium and Praseodymium.

$2NH_4NO_3.Pr(NO_3)_3$. Molec. wt., 486.82.

v.	Concentration.	Grams per liter.	$\mu_{v_{25°}}$.
0.8314	1.2027	568.40	134.1
1.6628	0.6013	284.20	248.0
3.3256	0.3006	142.10	334.9
8.314	0.1203	56.84	404.7
16.628	0.0613	28.42	451.1
33.256	0.03006	14.21	491.1
83.14	0.01203	5.684	531.3
166.28	0.006013	2.842	555.8
332.56	0.003006	1.421	580.3
831.8	0.001202	0.5684	613.2
1662.8	0.000601	0.2842	628.0
3325.6	0.000300	0.1421	642.8
8314.0	0.000120	0.0568	654.3

Table XVIII.—The Conductivity of Ammonium Praseodymium Nitrate Calculated for Even Volumes.

$2NH_4NO_3.Pr(NO_3)_3$.

v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.
1	157.0	20	459.2	400	585.0
2	265.6	40	496.5	800	604.0
4	344.3	80	528.8	1000	608.8
8	400.2	100	536.3	2000	631.0
10	413.9	200	560.8	4000	644.3

Praseodymium Nitrate.

This was made from the oxide by treatment with nitric acid and repeated (eight to ten times) evaporation to crystallization to remove all excess of acid.

The solution was standardized in the same manner as the double salt.

The volume of the solution was 2.6305, and its concentration 0.38015.

Table XIX.—Conductivity of Praseodymium Nitrate.

Praseodymium nitrate, $Pr(NO_3)_3$. Molec. wt., 326.58.

v.	Concentration.	Grams per liter.	$\mu_{v_{25^\circ}}$.
2.6305	0.38015	124.15	153.9
5.2610	0.19007	62.07	186.4
10.5220	0.09503	31.03	213.9
21.0440	0.04751	15.51	239.3
52.610	0.01900	6.207	270.9
105.22	0.00950	3.103	289.7
210.44	0.004751	1.551	308.2
526.1	0.001900	0.6207	336.4
1052.2	0.000950	0.3103	346.5
2104.4	0.000475	0.1551	359.7
5261.0	0.000190	0.06207	374.0
10522.0	0.000095	0.03103	396.0

Table XX.—Conductivity of Praseodymium Nitrate Calculated for Even Volumes.

$Pr(NO_3)_3$.

v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.
2	146.0	40	258.3	800	341.8
4	170.9	80	280.9	1000	345.9
8	200.8	100	288.6	2000	359.3
10	213.9	200	308.4	4000	370.6
20	236.8	400	325.2		

Ammonium Nitrate.

The substance used had been repeatedly crystallized, and dried to constant weight. The solution was then made up by weight.

Table XXI.—Conductivity of Ammonium Nitrate.

Ammonium nitrate, NH_4NO_3. Molec. wt., 80.12.

v.	$\mu_{v_{25^\circ}}$.	$2\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.	$2\mu_{v_{25^\circ}}$.
1	93.87	187.7	50	124.0	248.0
2	101.0	202.0	100	126.8	253.6
4	107.0	214.0	200	129.9	259.8
5	108.2	216.4	400	131.7	262.4
10	114.5	229.0	500	131.8	263.6
20	119.6	239.2	1000	137.2	274.4
40	123.5	247.0	2000	137.8	275.6

In the comparison of the conductivities, since the double salt has the composition $Pr(NO_3)_3.2NH_4NO_3$, we take twice the conductivity of the ammonium nitrate at one-half the dilution.

Table XXII.—Comparison. Ammonium Praseodymium Nitrate.

v.	$2\mu_{v_{25^\circ}}$ NH_4NO_3.	v.	$\mu_{v_{25^\circ}}$ $Pr(NO_3)_3$.	Sum.	$\mu_{v_{25^\circ}}$ Double salt.	Difference.
1	187.7	2	146.0	333.7	265.6	68.1
2	202.0	4	170.9	372.9	344.3	28.6
4	214.0	8	200.8	414.8	400.2	14.6
5	216.4	10	213.9	430.3	413.9	16.4
10	229.0	20	236.8	465.8	459.2	6.6
20	239.2	40	258.3	497.5	496.5	1.0
40	247.0	80	280.9	527.9	528.8	−0.9
50	248.0	100	288.6	536.6	536.3	+0.3
100	253.6	200	308.4	562.0	560.8	+1.2
200	259.8	400	325.2	585.0	585.0	0.0
400	262.4	800	341.8	604.2	604.0	+0.2
500	263.6	1000	345.9	609.5	608.8	+0.7
1000	274.4	2000	359.3	633.7	631.0	+1.3
2000	275.6	4000	370.6	646.2	644.3	+1.9

Double Nitrate of Ammonium and Neodymium.

The neodymium compounds at our disposal were the oxide, Nd_2O_3, and the nitrate, $Nd(NO_3)_3$. As the amount of substance available was not large enough, on account of the tremendous solubility of neodymium salts, to prepare a perfectly dry, double nitrate of neodymium and ammonium by crystallizing from a solution containing the constituents, we made solutions of the constituent nitrates, standardized them, and mixed them in proportions corresponding to the salt $2NH_4NO_3.Nd(NO_3)_3$.

It will be shown later, that such a mixture of salts is not necessarily exactly the same as a solution of the double salt itself, but its manner of ionization is not materially different, and at great dilutions the state of equilibrium is the same in the two cases.

It is obvious that this method of preparing the double salt is open to many objections. The least excess of either constituent will, of course, very materially change the conductivity. And since the equivalency of the quantities of the two solutions mixed is dependent upon the accuracy of both standardizations, the chance for error is comparatively large. We were not surprised, therefore, to find in the comparison of the dilute solutions, as will be seen in the table given below, that the "difference" did not become zero at great dilutions.

The neodymium nitrate was analyzed in the same general way as the praseodymium nitrate. On the addition of ammonium hydroxide a light-pink precipitate of the hydroxide came down. Since neodymium does not form any higher oxide than Nd_2O_3 on ignition in air, the precipitate was not ignited in a stream of hydrogen.

The solution was 0.8445 normal, and its volume 1.1840.

The solution of ammonium nitrate was made up by weight and contained 1 gram-molecule to the liter.

The solution of the double salt was prepared by bringing the constituents together in the proper proportions, and diluting the mixture in a measuring flask to a known volume. The double salt had a volume of 6.

Table XXIII.—Conductivity of the Double Nitrate of Ammonium and Neodymium.

Ammonium neodymium nitrate, $2NH_4NO_3.Nd(NO_3)_3$. Molec. wt., 489.96.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$.
6	0.1666	81.66	520.2
10	0.1000	48.996	570.9
20	0.0500	24.498	624.7
40	0.0250	12.249	674.0
80	0.0125	6.129	713.6
100	0.0100	4.8996	733.3
200	0.0050	2.4498	770.2
400	0.0025	1.2249	801.3

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}°$.
800	0.00125	0.6129	833.9
1000	0.00100	0.4899	850.2
2000	0.00050	0.2449	877.0
4000	0.00025	0.1224	884.8

Table XXIV.—Conductivity of Neodymium Nitrate.

Neodymium nitrate, $Nd(NO_3)_3$. Molec. wt., 329.72.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}°$.
1.184	0.8445	278.45	191.4
2.368	0.4222	139.22	282.0
4.736	0.2111	69.61	344.9
9.472	0.1055	34.80	393.0
23.68	0.0422	13.922	442.0
47.36	0.0211	6.961	475.6
94.72	0.0105	3.480	507.0
236.8	0.0042	1.3922	539.6
473.6	0.0021	0.6961	566.9
947.2	0.0010	0.3480	578.6
2368.0	0.0004	0.1392	599.9
4736.0	0.0002	0.0696	611.4

Table XXV.—The Conductivity of Neodymium Nitrate Reduced to Even Volumes.

$Nd(NO_3)_3$.

v.	$\mu_{v_{25}}°$.	v.	$\mu_{v_{25}}°$.	v.	$\mu_{v\ 5}°$.
1	187.2	20	429.4	400	558.8
2	253.5	40	466.0	800	575.1
4	325.4	80	497.3	1000	579.8
8	378.1	100	510.5	2000	594.5
10	394.8	200	531.2	4000	600.4

The conductivity of ammonium nitrate has been given above.

Table XXVI.—Comparison. Ammonium Neodymium Nitrate.

v.	$2\mu_{v_{25}}°$. NH_4NO_3.	v.	$\mu_{v_{25}}°$. $Nd(NO_3)_3$.	Sum.	$\mu_{v_{25}}°$. Double salt.	Difference.
5	216.4	10	394.8	611.2	570.9	40.3
10	229.0	20	429.4	658.4	624.7	33.7
20	239.2	40	466.0	705.2	674.0	31.7
40	247.0	80	497.3	744.3	713.6	30.7
50	248.0	100	510.5	758.5	733.3	25.2
100	253.6	200	531.2	784.8	770.2	14.6
200	259.8	400	558.8	818.6	801.3	17.3
400	262.4	800	575.1	837.5	833.9	3.8
500	263.6	1000	579.8	843.4	850.2	—6.8
1000	274.4	2000	594.5	868.9	877.0	—6.1
2000	275.6	4000	600.4	876.0	884.8	—8.8

It seems remarkable that the nitrates of two elements so closely related to each other as praseodymium and neodymium should possess such different electrical conductivities. That of neodymium nitrate is nearly 30 per cent larger than that of praseodymium nitrate. These salts are both exceedingly soluble in water and hygroscopic. Attention is called here, and, in a later portion of this paper, will be again called to the fact that, although the determination of the molecular lowering of the freezing-point of water by these substances does not increase regularly with increasing dilution, but shows a reentrant bend in the curve, nevertheless, the molecular conductivity increases regularly. The results show that ammonium praseodymium nitrate dissociates into its constituent molecules completely at about N/20 concentration, and thereafter behaves like a mixture of the constituent salts. The point of complete decomposition in the case of ammonium neodymium nitrate is at a volume of about 500.

Making use again of the data of Croustchoff and Peckhoff[1] for the conductivity of mixtures of electrolytes which do not form double salts, we find it recorded that the difference between the observed conductivity of the mixture and that calculated from the constituents amounts, in the case of the solution $\frac{1}{2}(KNO_3 + \frac{1}{2}Sr(NO_3)_2)$, to less than 1 per cent. The difference found in the results recorded here for ammonium praseodymium nitrate is 20 per cent for a volume 1, and for ammonium neodymium nitrate 10 per cent of the sum of the conductivities of the constituents.

There is, then, no doubt as to the existence of these nitrates at least partially undecomposed in concentrated solution. They soon dissociate into their constituents, however, and conduct themselves like mixtures of the single salts.

DOUBLE SULPHATES.

Double Sulphate of Ammonium and Magnesium.

The double salt was prepared by crystallization from a solution containing the constituent salts in equivalent proportions. The crystals were dried on absorbent paper and analyzed.

In the analysis of both the crystals and the solution of the double salt the magnesium was determined by precipitation with disodium phosphate.

---

[1] *Loc. cit.*

Analysis of the crystallized double salt:

	Calculated for $MgSO_4.(NH_4)_2SO_4.6H_2O$.	Found.
Mg	6.75	6.77

The strength of the solution used was 0.6215 normal, and its volume 1.6090.

Table XXVII.—Conductivity of the Double Sulphate of Ammonium and Magnesium.

Ammonium magnesium sulphate. Molec. wt., cryst., 360.76.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25°}}$.
1.609	0.6215	224.21	145.0
3.218	0.3107	162.10	187.7
6.436	0.1553	56.05	225.4
16.09	0.06215	22.42	265.5
32.18	0.03107	11.21	298.5
64.36	0.01553	5.605	333.4
160.9	0.006215	2.242	380.0
321.80	0.003107	1.121	409.4
643.60	0.001553	0.5605	443.9
1609.0	0.000621	0.2242	466.6
3218.0	0.000310	0.1121	494.3
6436.0	0.000155	0.0560	509.7

Table XXVIII.—The Conductivity of the Double Sulphate of Ammonium and Magnesium Calculated for Even Volumes.

$(NH_4)_2(SO_4).MgSO_4$.

v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.
1	128.9	20	273.5	400	417.8
2	155.4	40	306.9	800	447.5
4	196.9	80	340.9	2000	473.3
8	231.9	200	387.1		

The conductivity of magnesium sulphate has been determined by a number of experimenters—by Kohlrausch[1] and Krannhals[2] at 18°, and Walden[3] at 25°. The following values are taken from the work of these experimenters and are probably

[1] Wied. Ann., **26**, 161 (1885).

[2] Ztschr. phys. Chem., **5**, 250 (1890).

[3] *Ibid.*, **1**, 529 (1887).

quite accurate. The three sets of values did not differ very materially from one another when difference in temperature is taken into account.

Table XXIX.—Conductivity of Magnesium Sulphate.

Magnesium sulphate, $MgSO_4$. Molec. wt., 120.42.

v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.
2	62.6	80	139.3
4	76.7	200	165.9
8	89.1	400	184.3
20	110.0	800	199.5
40	123.4	2000	217.5

Ammonium Sulphate.

The material employed was carefully purified by repeated crystallizations.

The strength of the solution used was 0.1426 normal, and its volume 0.8751.

Table XXX.—Conductivity of Ammonium Sulphate.

Ammonium sulphate, $(NH_4)_2SO_4$. Molec. wt., 132.22.

v.	Concentration.	Grams per liter.	$\mu_{v_{25°}}$.
0.8751	1.1426	151.07	124.7
1.75	0.5713	75.53	143.6
3.50	0.2856	37.76	161.2
8.751	0.11426	15.107	182.2
17.50	0.05713	7.553	198.5
35.0	0.02856	3.776	215.0
87.51	0.011426	1.5107	235.3
175.0	0.005713	0.7553	248.3
350.0	0.002856	0.3776	260.9
875.1	0.001142	0.1510	269.5
1750.0	0.000571	0.0755	275.1

Table XXXI.—Conductivity of Ammonium Sulphate Calculated for Even Volumes.

$(NH_4)_2SO_4$.

v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.
1	127.4	20	199.9	400	261.7
2	146.1	40	216.9	800	268.3
4	163.2	80	232.4	2000	276.6
8	179.2	200	250.1		

Table XXXII.—Comparison. Ammonium Magnesium Sulphate.

v.	$\mu_{v_{25^\circ}}$. $MgSO_4$.	$\mu_{v_{25^\circ}}$. $(NH_4)_2SO_4$.	Sum.	$\mu_{v_{25^\circ}}$. Double salt.	Difference.
2	62.6	146.1	208.7	155.4	53.3
4	76.7	163.2	239.9	196.9	43.0
8	89.1	179.2	268.3	231.9	36.4
20	110.0	199.9	309.9	273.5	36.4
40	123.4	216.9	340.3	306.9	33.4
80	139.3	232.4	371.7	340.9	30.8
200	165.9	250.1	416.0	387.1	28.9
400	184.3	261.7	456.0	417.8	28.2
800	199.5	268.3	467.8	447.5	20.3
2000	217.5	276.6	494.1	473.3	20.8

Double Sulphate of Ammonium and Copper.

The double salt was prepared in the usual way, and crystallizes easily from the solution with 6 molecules of water of crystallization. The crystallized salt was dried on absorbent paper and analyzed.

Analysis $(NH_4)_2SO_4.CuSO_4.6H_2O$:

The copper was precipitated with alkali and weighed as oxide. The sulphuric acid was determined as barium sulphate.

	Calculated.	Found.
Cu	19.90	19.81
SO_4	48.04	47.78

The solution used was 0.5516 normal, and its volume 1.8128.

226.60 cc. of this solution were then diluted to 250 cc. to bring it to volume 2, and the dilutions were made from this as a mother-solution.

Table XXXIII.—Conductivity of the Double Sulphate of Ammonium and Copper.

Ammonium copper sulphate, $(NH_4)_2SO_4.CuSO_4$. Molec. wt., cryst., 400.0.

v.	Concentration.	Grams crystalized salt per liter.	$\mu_{v_{25^\circ}}$.
2	0.50	200.00	161.6
4	0.25	100.00	196.6
8	0.125	50.00	226.0
20	0.050	20.00	267.3
40	0.025	10.00	296.8

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25°}}$.
80	0.0125	5.00	331.0
200	0.0050	2.00	377.3
400	0.0025	1.00	406.9
800	0.00125	0.50	434.1
2000	0.00050	0.20	470.0

Copper Sulphate.

Kohlrausch[1] determined the conductivity of copper sulphate at 18°. We have used his results, changing them to values at 25° by means of the temperature coefficient 2.25, and have interpolated wherever necessary.

Table XXXIV.—Conductivity of Copper Sulphate.

Copper sulphate, $CuSO_4$. Molec. wt., 159.66.

v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.	v.	$\mu_{v_{25°}}$.
1	43.4	20	98.1	400	174.2
2	55.8	40	109.8	800	192.3
4	66.6	80	128.4	2000	219.8
8	74.5	200	156.2		

The conductivity of ammonium sulphate has already been given.

Comparison of the conductivity of ammonium copper sulphate with the sum of the conductivities of its single constituents is made below :

Table XXXV.—Comparison. Ammonium Copper Sulphate.

v.	$\mu_{v_{25°}}$. $(NH_4)_2SO_4$.	$\mu_{v_{25°}}$. $CuSO_4$.	Sum.	$\mu_{v_{25°}}$. Double salt.	Difference.
1	127.4	43.4	170.8		
2	146.1	55.8	201.9	161.6	40.3
4	163.2	66.6	229.8	194.6	35.2
8	179.2	74.5	253.7	220.0	33.7
20	199.9	98.1	298.0	266.8	32.2
40	216.9	109.8	326.7	296.8	29.9
80	232.4	128.4	360.8	330.8	30.0
200	250.1	156.2	406.3	377.3	29.0
400	261.7	174.2	435.9	406.9	29.0
800	268.3	192.3	460.6	434.1	26.5
2000	276.6	219.8	496.4	470.0	26.4

---

[1] Wied. Ann., **26**, 161 (1885).

Ammonium Ferrous Sulphate.

The substance used was the so-called "chemically pure" ammonium ferrous sulphate. It was found that the solution decomposed so quickly at 25° that the conductivity of only four dilutions was measured.

The solution was made up by weighing out the substance so as to have a concentration 0.5 normal. It was also standardized by precipitation with barium chloride.

The mother-solution had a volume 2.0003.

Table XXXVI.—Conductivity of Ammonium Ferrous Sulphate.

Ammonium ferrous sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$. Molec. wt., cryst., 392.40.

v.	Concentration.	Grams crystallized salt per liter.	$\mu v_{25°}$.
2	0.5	196.20	156.6
20	0.05	19.62	261.9
200	0.005	1.962	361.8
2000	0.0005	0.1962	466.5

The solution oxidized in the course of the measurements so that the results are not to be regarded as very accurate.

Ferrous Sulphate.

The ferrous sulphate used was made by dissolving an excess of iron (piano wire) in sulphuric acid. An excess of metal was present, while the solution was being concentrated. The substance was analyzed by precipitating the sulphuric acid.

The solution was 0.4664 normal, and its volume 2.1440.

Table XXXVII.—Conductivity of Ferrous Sulphate.

Ferrous sulphate, $FeSO_4$. Molec. wt., 152.06.

v.	Concentration.	Grams per liter.	$\mu v_{25°}$.
2.144	0.4664	70.92	59.8
21.44	0.0466	7.092	104.5
214.4	0.0046	0.7092	171.0
2144.	0.0004	0.07092	233.0

Table XXXVIII.—Conductivity of Ferrous Sulphate Calculated for Even Volumes.

$FeSO_4$.

v.	$\mu_{v25°}$.	v.	μ_{v25}.
2	59.4	200	170.6
20	104.0	2000	232.0

The conductivity of ammonium sulphate has already been given.

Comparison of the conductivity of ammonium ferrous sulphate with the sum of the conductivities of its constituents is given below:

Table XXXIX.—Comparison. Ammonium Ferrous Sulphate.

v,	$\mu_{v25°}$. $(NH_4)_2SO_4$.	$\mu_{v25°}$. $FeSO_4$.	Sum.	$\mu_{v25°}$. Double salt.	Difference.
2	146.1	59.4	205.5	156.6	48.9
20	199.9	104.0	303.9	261.9	42.9
200	250.1	170.6	420.7	361.8	58.9
2000	276.6	232.0	508.6	466.5	42.1

Double Sulphate of Ammonium and Cadmium.

The salt was prepared as usual, by crystallizing it from a solution of its constituents.

The crystallized salt, $(NH_4)_2SO_4.CdSO_4.6H_2O$, was dried on absorbent paper and analyzed. The cadmium was precipitated as carbonate and weighed as oxide in a Gooch crucible. The sulphuric acid was determined in the usual way.

Analysis of crystallized salt:

	Calculated for $(NH_4)_2SO_4.CdSO_4.6H_2O$.	Found. I.	II.
Cd	24.97	24.71	24.40
SO_4	42.84	42.80	42.76

The solution was 0.9888 normal, and its volume 1.0113. We then diluted 101.13 cc. to 200 to bring it to a volume of 2, and used this as a mother-solution in subsequent dilutions.

Table XL.—Conductivity of the Double Sulphate of Ammonium and Cadmium.

Ammonium cadmium sulphate, $(NH_4)_2SO_4.CdSO_4$. Molec. wt., cryst., 448.40.

v.	Concentration.	Grams per liter.	$\mu_{v_{25^\circ}}$.
2	0.50	224.20	151.6
4	0.25	112.10	185.0
8	0.125	56.05	216.0
20	0.050	22.42	254.4
40	0.025	11.21	285.5
80	0.0125	5.605	320.6
200	0.0050	2.242	366.2
400	0.0025	1.121	398.4
800	0.00125	0.5605	432.2
2000	0.00050	0.2242	474.0

Cadmium Sulphate.

The solution used was 1.3343 normal, and its volume 0.7496.

Table XLI.—Conductivity of Cadmium Sulphate.

Cadmium sulphate, $CdSO_4$. Molec. wt., 208.06.

v.	Concentration.	Grams per liter.	$\mu_{v_{25^\circ}}$.
0.75	1.3343	277.61	32.5
1.50	0.6671	138.80	45.5
3.00	0.3335	69.40	57.1
7.50	0.1334	27.76	71.8
15.00	0.0667	13.88	84.4
30.00	0.0333	6.94	99.8
75.00	0.0133	2.77	115.2
150.00	0.0066	1.39	130.0
300.00	0.0033	0.69	165.2
750.00	0.0013	0.27	190.5
1500.00	0.0006	0.14	209.2
3000.00	0.0003	0.07	225.7

Table XLII.—Conductivity of Cadmium Sulphate Calculated for Even Volumes.

$CdSO_4$.

v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.	v.	$\mu_{v_{25^\circ}}$.
1	36.8	20	89.6	400	170.8
2	49.4	40	103.1	800	191.7
4	60.4	80	122.5	2000	214.7
8	72.6	200	150.7		

The conductivity of ammonium sulphate has already been given.

Comparison of the conductivity of the double sulphate of ammonium and cadmium with the sum of the conductivities of its constituents, follows:

Table XLIII.—Comparison. Ammonium Cadmium Sulphate.

v.	$\mu_{v_{25°}}$ $(NH_4)_2SO_4$.	$\mu_{v_{25°}}$ $CdSO_4$.	Sum.	$\mu_{v_{25°}}$ Double Salt.	Difference.
2	146.1	49.4	195.5	151.6	43.9
4	163.2	60.4	223.6	185.0	38.6
8	179.2	72.6	251.8	216.0	35.8
20	199.2	89.6	289.5	254.4	35.1
40	216.9	103.1	320.0	285.5	34.5
80	232.4	122.5	354.9	320.6	34.3
200	250.1	150.7	400.8	366.2	34.6
400	261.7	170.8	432.5	398.4	34.1
800	268.3	191.7	460.0	432.2	27.8
2000	276.6	214.7	491.3	474.0	27.0

Double Sulphate of Ammonium and Nickel.

The salt employed was analyzed and found to be pure. The solution used had the concentration 0.1337 normal, and a volume of 7.4795. This was diluted to volume 8, and this solution employed as the mother-solution for subsequent dilutions.

Table XLIV.—Conductivity of the Double Sulphate of Nickel and Ammonium.

Ammonium nickel sulphate, $(NH_4)_2SO_4.NiSO_4$. Molec. wt., cryst., 395.10.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25°}}$.
8	0.125	49.39	224.1
20	0.050	19.755	263.4
40	0.025	9.877	293.8
80	0.0125	4.938	322.3
200	0.0050	1.9755	370.1
400	0.0025	0.9877	404.6
800	0.00125	0.4938	439.4
2000	0.00050	0.19755	484.6

Nickel Sulphate.

The solution used had a concentration of 0.2295 normal, and a volume 4.3570. 272.31 cc. were diluted to 500 cc. to bring it to a volume of 8, and this was used as the mother-solution for subsequent dilutions.

Table XLV.—Conductivity of Nickel Sulphate.

Nickel sulphate, $NiSO_4$. Molec. wt., 154.76.

v.	Concentration.	Grams per liter.	$\mu v_{25°}$.
8	0.125	19.34	77.9
20	0.050	7.738	96.1
40	0.025	3.869	109.0
80	0.0125	1.934	122.8
200	0.0050	0.7738	152.0
400	0.0025	0.3869	173.1
800	0.00125	0.1934	194.8
2000	0.00050	0.07738	232.3

The conductivity of ammonium sulphate has already been given.

Comparison of the conductivity of the double sulphate of nickel and ammonium, with the sum of the conductivities of its constituents, is given below:

Table XLVI.—Comparison. Ammonium Nickel Sulphate.

v.	$\mu v_{25°}$ $(NH_4)_2SO_4$.	$\mu v_{25°}$ $NiSO_4$.	Sum.	$\mu v_{25°}$ Double salt.	Difference.
8	179.2	77.9	257.1	224.1	33.0
20	199.9	96.1	296.0	263.4	32.6
40	216.9	109.0	325.9	293.8	32.1
80	232.4	122.8	355.2	322.5	32.9
200	250.1	152.0	402.1	370.1	32.0
400	261.7	173.1	434.8	404.6	30.2
800	268.3	194.8	463.1	439.4	23.7
2000	276.6	232.3	508.9	484.6	24.3

Double Sulphate of Potassium and Nickel.

The salt was made in the usual way by crystallization from a solution containing its constituents in equivalent proportions.

Analysis of crystallized $K_2SO_4.NiSO_4.6H_2O$:

	Calculated.	Found.
SO_4	43.93	43.82

The solution used was 0.1713 normal, and its volume 5.836. 364.75 cc. were then diluted to 500 cc. to bring it to volume 8, and this was employed as the mother-solution in subsequent dilutions.

Table XLVII.—Conductivity of Potassium Nickel Sulphate.

Potassium nickel sulphate, $K_2SO_4.NiSO_4$. Molec. wt., cryst., 435.24.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25^\circ}}$.
8	0.125	54.40	219.5
20	0.050	21.762	261.5
40	0.025	10.881	291.6
80	0.0125	5.440	323.7
200	0.0050	2.1762	369.4
400	0.0025	1.0881	400.2
800	0.00125	0.5440	438.0
2000	0.00050	0.21762	494.3

The conductivity of nickel sulphate has already been given. The conductivity of potassium sulphate has been determined by a number of observers. We take the values of Jones and Mackay[1] obtained for 25°.

Table XLVIII.—Conductivity of Potassium Sulphate.

Potassium sulphate, K_2SO_4. Molec. wt., 174.36.

v.	Concentration.	Grams per liter.	$\mu_{v_{25^\circ}}$.
8	0.125	21.795	182.4
20	0.050	8.718	205.1
40	0.025	4.359	220.3
80	0.0125	2.1795	237.9
200	0.0050	0.8718	252.4
400	0.0025	0.4359	262.2
800	0.00125	0.21795	273.0
2000	0.00050	0.08718	276.5

Comparison of conductivity of double sulphate of potassium and nickel, with the sum of the conductivities of its constituents, is next given:

Table XLIX.—Comparison. Potassium Nickel Sulphate.

v.	$\mu_{v_{25^\circ}}$ K_2SO_4.	$\mu_{v_{25^\circ}}$ $NiSO_4$.	Sum.	$\mu_{v_{25^\circ}}$ Double salt.	Difference.
8	182.4	77.9	260.3	219.5	40.8
20	205.1	96.1	301.2	261.5	39.7
40	220.3	109.0	329.3	291.6	37.7
80	237.9	122.8	360.7	323.7	37.0
200	252.4	152.0	404.4	369.4	35.0
400	262.2	173.1	435.3	400.2	35.1
800	273.0	194.8	467.8	438.0	29.0
2000	276.5	232.3	508.8	494.3	14.5

---

[1] Diss., Johns Hopkins University, 1896; This JOURNAL, 19, 83.

The results with double sulphates show that all of them remain undissociated to about the same extent. In a half-normal solution the "difference" amounts, in the case of ammonium magnesium snlphate, to 25 per cent; in ammonium copper sulphate to 29 per cent; in ammonium ferrous sulphate to 23 per cent; in ammonium cadmium sulphate to 22 per cent of the sum of the individual conductivities of the constituents. In the cases of nickel ammonium and nickel potassium sulphates the difference at a volume 8 about equals that of the other sulphates at the same dilution; more concentrated solutions were not measured, since these salts are not sufficiently soluble.

Klein[1] showed that a mixture of sodium and potassium sulphates has a conductivity which is about 1 per cent less than that calculated from its constituents. The difference here is much larger. Jones and Mackay[2] found a greater difference in the alums studied by them—from 2.5 to 11 per cent.

This would seem to indicate that the double sulphates which are not alums exist to a greater degree undissociated in aqueous solution than the alums. The difference was found to disappear at a dilution of about 400 liters in the case of the alums, while in the case of the sulphates under investigation it did not disappear at a dilution of 2000.

DIRECT COMPARISON OF DOUBLE SALT AND MIXTURE.

Through the work referred to in this paper the conclusion has been reached that double salts in concentrated solution dissociate to a greater or less extent as if they were salts of complex acids, and then, as the dilution increases, the complex ion dissociates into simpler ions.

The question now arises, is the state of equilibrium the same in a solution of a double salt as it is in a mixture of solutions of the constituents having the same concentration as the double salt? It seemed desirable to test this question as thoroughly and carefully as possible. Mr. C. F. Lindsay[3] has already obtained some very interesting results bearing on this problem. He found that the conductivities of mixtures of the constituents were always slightly larger than those of the double salt at the same dilution. On account of the very unexpected and surprising results obtained, we have repeated some of his work, and also studied the question with other substances.

---

[1] Wied. Ann., **27**, 151.

[2] *Loc. cit.*

[3] This JOURNAL, **25**, 62.

The method of work was the same as that described above. The solution of the double salt was carefully standardized and the conductivity determined. Then a solution of each of the constituent salts was prepared and accurately standardized. From these analyses the volumes of the two solutions, which would contain the salts in the same proportion in which they exist in the double salt, were calculated. These volumes of the two solutions were mixed in a measuring flask, and the whole diluted to a known volume. This mixture was then standardized gravimetrically to see that no error had been made in bringing the constituents together and in the dilution. This standardized solution, which in every case was found to contain the constituents to almost exactly the extent calculated, was used as the mother-solution in subsequent dilutions.

The same cell was used to measure the conductivity of the double salt as was employed with the mixture, and they were generally measured as nearly as possible at the same time, in order that the temperature of the thermostat (which was regulated within 0°.1 by an Ostwald regulator) might be the same. The same apparatus was used throughout with the double salt and the mixture.

Lindsay obtained the following results:

Table L.—Double Chloride of Potassium and Cadmium.

$KCl.CdCl_2$.

v.	Double salt, $KCl.CdCl_2$. μ_v.	Mixture, $KCl + CdCl_2$. μ_v.	Difference.
2	117.8	119.4	1.6
4	146.3	148.1	1.8
8	172.4	174.9	2.5
20	208.4	209.3	0.9

The conductivity of the double chloride is, thus, less than the conductivity of the mixture of the two chlorides. The difference in this case and in all other cases tried, is always small, but is larger than all known experimental errors, and is always in the same direction; *i. e.*, the mixture has the higher conductivity.

Table LI.

Double sulphate of potassium and nickel, $K_2SO_4.NiSO_4$.

v.	Double salt. $K_2SO_4.NiSO_4$. μ_v.	Mixture. $K_2SO_4.NiSO_4$. μ_v.	Difference.
6	213.68	216.31	2.63
12	244.38	246.61	2.23
24	273.31	276.02	2.71
60	314.13	314.35	0.22

Table LII.

Double sulphate of ammonium and magnesium, $(NH_4)_2SO_4.MgSO_4$.

v.	Double salt. $(NH_4)_2SO_4.MgSO_4$. μ_v.	Mixture. $(NH_4)_2SO_4 + MgSO_4$. μ_v.	Difference.
2	159.7	164.6	4.9
4	197.7	202.4	4.7
8	231.5	237.1	5.5
20	273.9	277.9	4.0

We repeated the work of Lindsay with ammonium magnesium sulphate, and also studied in this connection ammonium cadmium sulphate. We obtained the following results:

Table LIII.

Ammonium magnesium sulphate, $(NH_4)_2SO_4.MgSO_4$.

v.	Double salt. $(NH_4)_2SO_4.MgSO_4$. μ_v.	Mixture. $(NH_4)_2SO_4 + MgSO_4$. μ_v.	Difference.
5.09	212.70	216.78	4.08
10.18	243.89	248.28	4.39
25.46	284.80	289.10	4.30
Repeated, making and standardizing solutions anew.			
3.09	189.9	193.2	3.3
Repeated, making and standardizing solutions anew.			
6.064	216.03	219.96	3.93

Table LIV.

Ammonium cadmium sulphate, $(NH_4)_2SO_4.CdSO_4$.

v.	Double salt, $(NH_4)_2SO_4.CdSO_4$. μ_v.	Mixture, $(NH_4)_2SO_4 + CdSO_4$. μ_v.	Difference.
3.036	171.94	173.25	1.31
3.001	171.7	172.4	0.7

From these results the conclusion is reached that the conductivity of a double salt in concentrated solutions is slightly less than the conductivity of a mixture of the constituents having the same concentration as the double salt. It thus appears fairly certain from the work of Lindsay and from our own, that the double salt, when once formed, does not dissociate in exactly the same way or to the same extent as the mixture of the constituents which have never united to form the double salt.

CRYOSCOPIC MEASUREMENTS.

The application of the freezing-point method to the problem of the condition of double salts in solution has already been made by several. Jones and Mackay[1] found from the study of the alums results which led to the same general conclusions as those obtained by the conductivity method. Jones and Ota attempted to apply the freezing-point method to solutions of double chlorides, but obtained results of an entirely unexpected character. The molecular conductivities beyond a certain concentration increased with the concentration to a very marked extent. Phenomena similar to these have since been studied by Jones and Chambers,[2] and later by Chambers and Frazer.[3]

We have applied the freezing-point method to a number of the substances whose conductivities we have studied in order to see whether normal values would be obtained, or whether they would give such apparently abnormal results as had been obtained by Jones and Chambers, and by Chambers and Frazer. The following results were obtained with the double cyanide of potassium and mercury :

---

[1] *Loc. cit.*

[2] This JOURNAL, **23**, 89.

[3] *Ibid.*, **23**, 512.

Table LV.—Double Cyanide of Potassium and Mercury, $K_2Hg(CN)_4$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
2.442	156.74	0.4095	1°.902	4.64
4.884	78.37	0.2047	0°.971	4.74
12.210	27.35	0.0819	0°.405	4.94

Table LVI.—Mercuric Cyanide, $Hg(CN)_2$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
5	50.476	0.2	0°.387	1.93

Table LVII.—Potassium Cyanide, KCN.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
1.1034	59.08	0.9063	3°.385	3.73
1.4343	45.45	0.6972	2°.623	3.76
2.8686	22.72	0.3486	1°.321	3.79
7.4129	8.79	0.1349	0°.531	3.93

Table LVIII.—Comparison. Potassium Mercuric Cyanide.

v.	2Δ KCN.	*v.*	Δ $Hg(CN)_2$.	Sum.	Δ Double salt.	Difference.
2.5	7.57	5	1.93	9.50	4.73	4.77

In the above and following results *v* is the volume of the solution, L the lowering of the freezing-point actually observed, and Δ the molecular lowering of the freezing-point.

The freezing-point lowerings of this double salt and its constituents are normal; *i. e.*, the molecular lowerings increase from the most concentrated to the most dilute solutions.

Table LIX.—Potassium Cadmium Iodide, K_2CdI_4.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
2.302	303.08	0.4344	3°.878	8.927
2.762	252.56	0.362	3°.177	8.776
5.524	126.28	0.181	1°.557	8.602
9.207	75.77	0.1086	0°.960	8.84
13.810	50.51	0.0724	0°.664	9.17

This salt shows a minimum in the curve of molecular depressions between the volumes 2.7 and 5.5 or between the volumes 5.5 and 9.2. The comparison with its constituents was therefore not attempted, and the molecular depressions produced by the constituents were not ascertained.

These results are strikingly analogous to those already found. The molecular lowering decreases with the dilution up to a certain point, reaches a minimum, and then increases from this point with further increase in dilution. The concentration at which this minimum was observed in the molecular lowering was found to vary somewhat with the nature of the substance, but it usually occurred at a dilution of from 0.1 to 0.2 normal. It occurs at this same concentration in the double iodide, as can be seen from Table LIX.

RESULTS WITH SULPHATES.

Table LX.—Ammonium Cadmium Sulphate,
$(NH_4)_2SO_4.CdSO_4$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
1.6347	202.03	0.6117	3°.052	4.99
2.0433	161.64	0.4894	2°.493	5.09
2.7248	121.11	0.3670	1°.914	5.21
4.0866	80.82	0.2447	1°.345	5.49
8.1732	40.41	0.1223	0°.719	5.88
16.3464	20.20	0.0612	0°.378	6.17

Table LXI.—Cadmium Sulphate,
$CdSO_4$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
0.7502	277.30	1.3328	2°.526	1.89
1.0004	207.97	0.9996	1°.774	1.77
1.5004	138.64	0.6664	1°.175	1.73
1.876	110.89	0.533	0°.933	1.75
2.500	83.22	0.400	0°.714	1.78
3.752	55.13	0.2665	0°.505	1.89
7.504	27.56	0.1333	0°.263	1.93

Table LXII.—Ammonium Sulphate, $(NH_4)_2SO_4$.[1]

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
5.0	26.432	0.2	0°.829	4.14
10.0	13.216	0.1	0°.437	4.37
14.28	9.2512	0.07	0°.316	4.51
20.00	6.608	0.05	0°.237	4.74
33.33	3.9648	0.03	0°.148	4.93
66.66	1.9824	0.015	0°.075	5.00

Table LXIII.—Comparison. Ammonium Cadmium Sulphate.

v.	Δ $CdSO_4$.	Δ $(NH_4)_2SO_4$.	Sum.	Δ Double salt.	Difference.
5	1.90	4.14	6.04	5.57	0.47

Table LXIV.—Ammonium Copper Sulphate, $(NH_4)_2SO_4.CuSO_4$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
3.069	130.32	0.3258	1°.736	5.32
6.138	65.16	0.1629	0°.990	6.07

Of the sulphates studied, only cadmium sulphate shows a minimum in the molecular lowering of the freezing-point.

DOUBLE NITRATE OF PRASEODYMIUM AND AMMONIUM.

Table LXV.—Praseodymium Nitrate, $Pr(NO_3)_3$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
2.6305	124.15	0.38015	2°.184	5.74
5.2610	62.07	0.19007	1°.054	5.53
10.5220	31.03	0.09503	0°.543	5.71
21.0440	15.51	0.04752	0°.284	5.97

This salt does not give a regular rise in the molecular depression with increasing dilution, but decreases, reaching a minimum between the volumes 2 and 10. It therefore falls in the same category with those salts described by Jones and Chambers.[2]

---

[1] Jones and Mackay: *Loc. cit.*

[2] This JOURNAL, **23**, 89.

Table LXVI.—Molecular Lowering of Praseodymium Nitrate Calculated for Even Volumes.

v.	Concentration.	Molecular lowering. Δ.
2	0.5	5.79
4	0.25	5.63
8	0.125	5.63
20	0.050	5.95

Table LXVII.—Ammonium Nitrate,
NH_4NO_3.

v.	Concentration.	Grams per liter.	Lowering. L.	Molecular depression. Δ.	Twice the molecular depression. 2Δ.
1	1.0	80.12	3°.136	3.13	6.27
2	0.5	40.06	1°.629	3.26	6.52
4	0.25	20.03	0°.863	3.45	6.90
10	0.10	8.012	0°.363	3.63	7.26

Table LXVIII.—Ammonium Praseodymium Nitrate,
$2NH_4NO_3.Pr(NO_3)_3$.

v.	Concentration.	Grams per liter.	Lowering L.	Molecular depression. Δ.
0.8314	1.2027	568.40	16°.5	13.71
1.6628	0.6013	284.20	7°.5	12.47
3.3256	0.3006	142.10	3°.637	12.09
8.314	0.12027	56.84	1°.779	14.79
16.628	0.06013	28.42	0°.887	14.79

This double salt exhibits the minimum in the molecular depression. As this is not observed in the case of ammonium nitrate, and is observed in praseodymium nitrate, we must ascribe it to the influence of the praseodymium nitrate.

Table LXIX.—Molecular Depression of Ammonium Praseodymium Nitrate Calculated for Even Volumes.

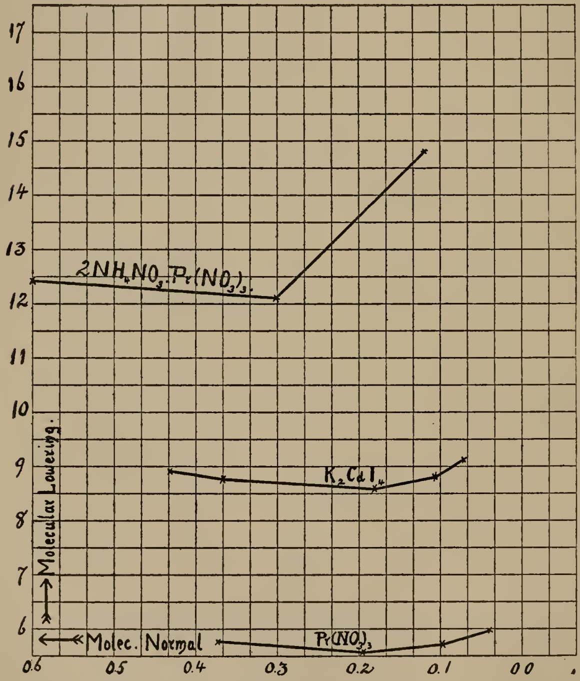
v.	Concentration.	Molecular depression. Δ.
2	0.5	12.40
4	0.25	12.45
8	0.125	14.63
20	0.050	

Table LXX.—Comparison. Ammonium Praseodymium Nitrate.

v.	2Δ NH_4NO_3.	*v.*	Δ $PrNO_3$.	Sum.	Δ. Double salt.	Difference.
1	6.27	2	5.79	12.06	12.40	—0.36
2	6.52	4	5.63	12.15	12.45	—0.30
4	6.90	8	5.63	12.53	14.63	—2.10
10	7.26	20	5.95	13.21		

A minimum in the molecular lowering exists in praseodymium nitrate at a concentration of about 0.2 normal. A minimum occurs in the molecular lowering of the double nitrate at about the same concentration, as has been pointed out.

In order that these minima in the molecular lowering may be seen more clearly, some of our results are plotted in curves. The ordinates are molecular lowerings and the abscissas are concentrations.



Jones and Chambers[1] have offered a possible explanation of these minima in the freezing-point curves. Since the molecular lowerings in the very concentrated solutions are much larger than would be expected, they suggest that in these concentrated solutions the dissolved substance has combined with a portion of the solvent, forming compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The total amount of the solvent present is diminished by just so much as has combined with the dissolved substance. The freezing-point lowering is abnormally great because a part of the water is no longer present as solvent, but is in combination. They refer to a number of cases where definite compounds between water and the dissolved substance are known to exist in concentrated solutions.

---

[1] This JOURNAL, 23, 103.

It is impossible to say at present whether or not this explanation is the true one. We accept it tentatively, as we are not prepared to offer any other theory to account for the facts.

SUMMARY.

We are led from the results of the study of the electrical conductivity of the solutions investigated, to the conclusion that the double iodides of strontium and cadmium and of potassium and cadmium exist in concentrated solution to a considerable extent undecomposed. They do not break down very readily, but retain their compound nature even at moderately high dilutions. The same thing is found to be true of the double nitrates of ammonium with praseodymium and neodymium, and of the double cyanide of potassium and mercury. The nitrates, however, break down at comparatively low dilutions. The double sulphates of ammonium with cadmium, copper, magnesium, iron, nickel, as well as that of potassium and nickel, appear not only to remain undissociated to some extent in concentrated, but even in dilute solutions they are not completely dissociated into their constituents.

A study of the conductivities of certain mixtures and double salts showed that the state of equilibrium is not necessarily always the same in the two cases at the same concentration. While the double salt may not be completely dissociated into its constituents at any given dilution, the constituents do not combine to form the same amount of double salt when brought together at that dilution.

Cadmium sulphate, potassium cadmium iodide, praseodymium nitrate, and ammonium praseodymium nitrate, are substances whose molecular lowering of the freezing-point of water does not increase regularly with the dilution, but there exists a well-defined minimum in the molecular lowering, and this occurs for each of the above substances at a dilution not widely removed from 0.2 normal. As the concentration increases from this point the molecular lowering may increase very considerably.

We had hoped to electrolyze solutions of the double salts employed in this work, to determine if possible the nature of the complex anions. We propose to carry out such an investigation in the future.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January, 1901.

Contribution from the Labratory of General Chemistry, University of Michigan.

ON THE CONSTITUENTS OF JAMAICA DOGWOOD.

BY PAUL C. FREER AND A. M. CLOVER.[1]

The Jamaica dogwood (*Piscidia Erythrina*, *Linné*) is a tree, usually about 20 feet in height, belonging to the order of Leguminosae, having its habitat in the West Indian Islands and adjacent mainland. The portion used is the bark of the root, and the active principle was supposed to be a resinoid called piscidine, which was said to crystallize from alcohol in colorless prisms, melting at 192°. As will be shown below, this principle, in reality, is not a chemical individual, but it consists of two very distinct bodies.

The material used in the investigation was the pulverized bark of the root and, of the series of extracts, that with water contained the greatest quantity of solid matter, this solution, the chief portion of the residue of which is the calcium salt of a new acid, will therefore be considered first.

Aqueous Solution—Piscidic Acid.

The pulverized bark was placed in 10-gallon crocks, about

---

[1] Parke, Davis & Co. Fellow in the University of Michigan. This work was undertaken with materials furnished by Messrs. Parke, Davis & Co. and at their suggestion, in order to clear up the chemistry of a most interesting plant, from a purely scientific standpoint. Our thanks are due to Messrs. Parke, Davis & Co. for their willing assistance and unflagging interest.

10 pounds to each vessel. It was then covered with pure water and allowed to stand for three or four days, being thoroughly stirred from time to time, and finally the liquid was siphoned off, this operation being repeated until no further substance went into solution. The united, straw-colored extract was then gently evaporated on a water-bath until it had diminished to one-fourth of its original bulk. Samples of this concentrated extract, when evaporated to dryness, demonstrated the presence of a very deliquescent calcium salt of an organic acid. This calcium salt can be separated from the concentrated aqueous solution by the addition of alcohol, in which it is insoluble, and filtering the precipitate. After heating with water containing animal charcoal, it can, on evaporation, be separated in colorless crystals, from which the pure acid can be obtained by solution in water, precipitation with lead acetate, decomposition of the white lead salt with hydrogen sulphide in alcoholic suspension, and evaporation of the solution. However, this method is rather tedious, and it also involves the use of considerable alcohol, so that it is better, although it does not at first yield so pure an acid, to proceed as follows: The concentrated aqueous solution is first precipitated with a solution of lead acetate in sufficient quantity to separate all of the coloring-matter along with the lead salt of a portion of the acid. This brownish precipitate is filtered and the clear filtrate once more precipitated with lead acetate, care being taken not to separate all of the acid in this way, as the very last portions of the lead salt are impure. The nearly pure lead salt is washed repeatedly by decanting with water. It is finally poured on a large suction-filter and dried as well as possible. As it filters with great difficulty, it is advisable to have as little liquid as possible during this last stage. The lead salt is finally suspended in a sufficient quantity of alcohol to make a thin paste and completely decomposed with hydrogen sulphide. The alcoholic solution, after filtering, is first concentrated by distilling off the alcohol *in vacuo*, until the bulk has decreased to about one-sixth. It is then placed in large dishes and evaporated in the cold. There remains a thick syrup, which is sometimes permeated with a few crystals (ethyl ether of the acid), the whole finally solidifying to

a mass of radiating needles. The acid is extremely soluble in water, slightly so in ether; insoluble in chloroform, benzene, and ligroin.

In order to purify the substance it is placed in a Soxhlet extractor and exhausted with ether, when an insoluble residue, consisting mainly of calcium salt, remains. The ethereal solution, on evaporation, is free from inorganic residue, and deposits the acid in sticky lumps somewhat resembling glucose. This remainder is then dissolved in a little alcohol, about twice the volume of ether added, and chloroform poured in until precipitation begins. On scratching the sides of the flask with a glass rod, feathery concentric crystals are deposited, the melting-point of which is 182° to 185°, decomposition, with evolutions of carbon dioxide, beginning at 185°. For analytical purposes, the acid was recrystallized from methylpropylketone, which seems to be the only solvent from which it is at once deposited in crystals on cooling. The crystals obtained from the latter solvent, however, retain methylpropylketone very obstinately, so that the last traces can be expelled only by continued heating at 110° to 120°.

The samples analyzed were recrystallized three times from methylpropylketone and dried at 110°.

I. 0.2091 gram substance gave 0.3941 gram CO_2; and 0.0910 gram H_2O.

II. 0.1880 gram substance gave 0.3524 gram CO_2; and 0.0836 gram H_2O.

	Calculated for $C_{11}H_{12}O_7$.	Found. I.	II.
C	51.5	51.45	51.11
H	4.7	4.84	4.93

No account of an acid of this composition, with the properties of ours, has been found in the literature, so that we have given to the one above described the name piscidic acid.

The properties of piscidic acid are very much like those of mucic or saccharic acid. It decomposes on heating, giving an odor of caramel, and finally chars, leaving a porous coke. It is instantly oxidized by potassium permanganate, forming potassium carbonate, oxalate, and apparently formate, so that complete destruction of the molecule takes place.

Piscidic acid is dibasic, as is shown by the following experiment:

N/8 NaOH solution was just neutralized with pure recrystallized acid, the conductivity (equivalent) determined at N/32 and N/1024.

	Bridge.	Resistance out.	T. 25°, equiv. acid.
λ_{32}	426.4	100	
	450.6	110	λ 68.9
	493.0	130	
λ_{1024}	474.6	3000	λ 88.8
	499.2	3300	
	507.0	3400	λ 89.2

$$\frac{\lambda_{1024}-\lambda_{32}}{10} = 2.0+.$$

According to Ostwald's law[1] the acid is consequently dibasic. The acid value gave the following results:

1. 0.3503 gram substance took 27.4 cc. N/10 KOH to neutralize it.

Equivalent weight = 128; molecular weight = 256.

2. Determined from different sample: 0.3390 gram substance took 25.9 cc. N/10 KOH.

Equivalent weight = 130.8; molecular weight = 251.6; Calculated molecular weight, 256.

It is evident that a combination of basicity determinations by means of the electric conductivity, and of the acid value of any acid must give the molecular weight.

Piscidic acid is therefore a dibasic acid and evidently contains two carboxyl groups, as the following experiment shows:

0.5 gram of the acid were mixed with 0.5 gram resorcin and then heated in an oil-bath to 180° for fifteen minutes. 0.2 gram freshly fused zinc chloride was then added to the mass, and the temperature gradually increased to 210°, where it was kept for half an hour. When cold, the product was taken out, washed with hydrochloric acid, and finally a trace dissolved in caustic soda and diluted with water. The result was an intense fluorescence. The two carboxyl groups evidently must be in the γ, γ' positions as in phthalic or succinic acids. The resulting formula of the acid is, therefore,

$$C_9H_{10}O_3(CO_2H)_2.$$

---

[1] Ostwald: Ztschr, phys. Chem., 1, 74; 2, 901.

Ethyl Ester—Three grams of piscidic acid were dissolved in absolute alcohol, 10 drops of hydrochloric acid added, and the whole boiled on the water-bath for two or three hours, the alcohol was then gently evaporated and the whole allowed to crystallize. The ester was recrystallized from hot water. It separated in shiny needles, melting at 207°–208°, softening at 204°. This substance is the acid ester, as is shown by the fact that it dissolves in sodium carbonate, and this is a further proof of the relative positions of the two carboxyl groups. The same ester is formed in limited quantities during the original isolation of the acid, provided hydrochloric acid is present during the extraction, the alcohol necessary being present during the precipitation of the lead salt with hydrogen sulphide.

I. 0.2240 gram substance gave 0.4579 gram CO_2; and 0.1134 gram H_2O.

II. 0.1976 gram substance gave 0.4010 gram CO_2; and 0.988 gram H_2O.

	Calculated for $C_{13}H_{16}O_7$.	Found. I.	II.
C	54.9	55.02	55.34
H	5.6	5.62	5.56

The acid value of the ester confirms this analysis:

0.6139 gram substance took 43.4 cc. of N/10 potassium hydroxide to neutralize it after heating on a water-bath for one-half hour.

Calculated molecular weight, 284; found molecular weight, 283.

The substance, after saponification as above, was treated with the equivalent quantity of sulphuric acid, evaporated to dryness, and the residue extracted with a little alcohol, ether, and chloroform; and stood aside to crystallize. The result was the production of the original acid.

The acid ester was boiled with absolute alcohol and sulphuric acid for several hours, but no further change took place; the neutral ester cannot be produced in this way.

Aniline Salt and Anilide.—Two grams of acid in 10 cc. of alcohol were treated with 1.5 grams of aniline, and gently warmed for a few minutes. On standing, shiny, white plates of the aniline salt crystallize (melting-point 149°). This salt, heated for two hours at 170° to 180°, gives off water and leaves a thick syrup, which cools to a resinous mass. On being covered with alcohol, it dissolves gradually and a white solid is precipitated on standing. Recrystallized from alcohol and water, and finally from ether, it separates in white needles, melting at 196°.

I. 0.1439 gram substance gave 0.3600 gram CO_2; and 0.0729 gram H_2O.

II. 0.1476 gram substance gave 0.3693 gram CO_2; and 0.764 gram H_2O.

III. 0.197 gram substance gave 13 cc. N at 23° and 733 mm.

	Calculated for $C_{23}H_{22}N_2O_5$.	Found. I.	II.	III.
C	67.98	68.23	68.24	....
H	5.42	5.63	5.42	....
N	6.89	....	....	7.09

This substance is therefore the dianilide. A molecular weight determination, by the boiling-point method in ethyl alcohol gave results showing a gradual rise in molecular weight with increased amount of substance, results in accord with Auwers' experience with anilides and hydroxy-compounds.[1]

Solvent.	Substance.	Δ.	M.	Calc. M.
17.496	0.558	0.097	378.2	406
	1.151	0.189	400.7	
	1.798	0.285	415.0	
	2.347	0.366	421.7	

A neutral solution of piscidic acid is not precipitated by copper or barium salts; mercuric salts precipitate slightly yellow, silver nitrate white, the silver salt rapidly turning black. The lead salt is white and stable.

In order to learn more in regard to the constitution of the acid, it was heated with hydriodic acid, in order to determine methoxy groups according to Zeisel's method, but with entirely negative results, no methoxy groups being present. The acid was finally heated in a sealed tube to 100° with hydriodic acid (sp. gr. 1.96) without producing methyl iodide. The reaction-product consisted for the greater part of oily and tarry substances from which only a small quantity of a solid substance, in yellow needles, melting at 120°, could be isolated, the quantity being too little for analysis. Hydrobromic acid (sp. gr. 1.12) even at 150° for several hours, seems to have no effect, the unchanged acid being recovered. It is therefore safe to assume that no saponifiable groups are present.

---

[1] Ztschr. phys. Chem., **23**, 449; **30**, 529.

In order to ascertain the number of hydroxyl groups present, attempts were made to obtain an acetyl derivative of the acid; however, the resulting substance was an oil which could not be crystallized. Better results were obtained with the ethyl ester.

Three and a half grams ethyl ester were covered with 20 grams of pure acetic anhydride, sealed in a tube, and heated for five hours at 100°. After cooling, the tube contained a clear, slightly yellow liquid. This was added to water and the water gradually neutralized in the cold with sodium carbonate, finally in excess. There remained a small quantity (0.75 gram) of an insoluble thick resin, the remainder dissolved. The colorless solution was filtered through wet filter paper and exhausted with ether. It was then acidified and again extracted with ether, dried over calcium chloride, evaporated to three-quarters, and then placed in a crystallizing dish in a vacuum. There remained a colorless resin which, on being covered with dry ether and rubbed with a glass rod, finally crystallized in white, rhombic flakes, melting at 149° to 151°.

0.1449 gram substance gave 0.2953 gram CO_2; and 0.0717 gram H_2O.

	Calculated for $C_{17}H_{20}O_9$.	Found.
C	55.4	55.6
H	5.4	5.4

I. 0.5272 gram substance took 14.0 cc. N/10 KOH to neutralize it.

II. 0.5430 gram substance took 14.3 cc. N/10 KOH to neutralize it.

Calculated molecular weight 368; found 376 and 379.

For saponification, an excess of a N/10 potassium hydroxide was added, and the whole warmed. On completion of the reaction it was found, however, that the caustic potash used was far in excess even of that called for by five acetyl groups, an obvious impossibility, so that the conclusion was reached that potash in excess decomposes the acid completely. A determination of acetyl groups with baryta gave results which agreed approximately with two acetyl groups, but these were too low. There cannot be much doubt that this is a diacetyl derivative.

Fusion of the acid with potash resulted in complete decomposition, no satisfactory results being obtained. The acid evidently does not contain an aromatic group, its extreme solubility in water, its resemblance to saccharic acid, the impossibility, so far, of isolating an aromatic derivative from it, all speak in favor of its being a member of the aliphatic series.

Bromine, in absolute chloroform solution, attacks the acid slowly; apparently no addition-product is produced, as hydrobromic acid is given off from the start. In aqueous solution, bromine reacts steadily. Two grams of the acid were dissolved in as little water as possible, and then bromine water added gradually until a permanent color appeared. The solution was then evaporated at ordinary temperatures, under which conditions colorless prisms separated, which, recrystallized from water, yield silky, concentric needles, melting at 234° to 236°, with decomposition and separation of hydrobromic acid. The analyses agree best with the figures calculated for a dibromine addition-product, and not for a body produced by substitution.

	Calculated for		
	$C_{11}H_{10}O_7Br_2$.	$C_{11}H_{12}O_7Br_2$.	Found.
C	31.8	31.7	30.91
H	2.39	2.85	2.75
Br	38.6	38.4	37.58

The quantity of acid at our disposal was not sufficient to enable us to carry on experiments which would settle the constitution of piscidic acid definitely, but we hope at some future time again to take up the subject of this interesting acid and definitely settle its structure. Its structure, as far as is yet known, is represented by $C_9H_8O(OH)_2(CO_2H)_2$.

EXTRACTS FROM THE BARK OF JAMAICA DOGWOOD WITH SOLVENTS OTHER THAN WATER.

Chloroform Extract.

Chloroform extracts all of the crystalline constituents of the Jamaica dogwood bark, excepting piscidic acid and one other body, which occurs in the solution formed with ligroin. Amorphous substances, mainly consisting of cutose, are not taken up by the solvent, and, as a consequence, the individual substances can be isolated in a pure state. The methods of isolation of the various products will be described first, the properties and reactions subsequently.

Fifteen pounds of ground bark were thoroughly exhausted with chloroform; 90 grams of residue, which solidified on cooling, remaining after evaporating the solvent on a water-bath. This residue was dissolved in 400 cc. of chloroform and allowed to stand for several days. A white precipitate (8 grams) deposited in the bottom of the flask. This was filtered, washed well with chloroform, and dried. It contained a body which, when pure, melts at 150° to 155°.

The chloroform filtrate was evaporated to half of its original volume, diluted with an equal volume of ether, and then extracted with caustic potash (100 grams to 300 cc. of water), the whole being carefully cooled. The caustic potash solution turns deep-red, and takes up over one-half of the contents of the chloroform-ether. The latter was repeatedly washed with water until this solvent became colorless, then with a trace of acid, finally dried over calcium chloride, and ether-chloroform distilled. The residue obtained in this way will be described first, the alkaline extract second.

A. Neutral Residue from Ether-Chloroform Extract.—After distilling off the chloroform the residue, after extraction with caustic potash, was covered with 200 cc. of ether. Crystallization soon begins and continues for several hours. The residue is then filtered and well washed with ether. The crystals (10 grams), after being dried on a porous plate, were purified further by boiling out with about a liter of ligroin, a white amorphous substance being removed thereby. The remainder now consisted of two bodies which could be separated by fractional crystallization as follows: A hot alcoholic solution of the two is allowed to cool without stirring; one of the bodies, melting at 216°, then separates before the other, and can be filtered, the other finally coming down on longer standing (melting-point 201°).

The body melting at 216° consists of yellow, light, and very fine needles; that melting at 201° consists of colorless, heavy prisms. The proportions are one to five.

Ether Solution Filtered from the Substances that Melt at 201° and 216°.—After distilling the solvent, the residue weighed 25 grams. It was dissolved in 100 cc. of ether and allowed to stand over calcium chloride. When dry, it was treated with about five volumes of ligroin, the flask being well shaken during the addition. A precipitate is formed which settles to the bottom in a slightly caked condition, so that the supernatant liquid can be decanted; afterward, the precipitate is rendered perfectly granular by shaking with a small quantity of ligroin.[1] Quantity, 10 grams.

The solvent, after filtration, was concentrated and completely freed from volatile matter. It was then washed with 70 per cent alcohol (which removed some of the substance melting at 50° to 80° mentioned in the foot-note), and finally heated in a pressure-flask with alcoholic potash at 100° for several hours. The alcoholic solution, when evaporated and extracted with ether, yielded a considerable quantity of non-saponifiable matter[4] which crystallized from alcohol in colorless flakes, melting at 123° to 125°, probably some complex alcohol formed during saponification. The ethereal mother-liquors deposited a further quantity of substance on fractional crystallization, together with a considerable quantity of amorphous matter, which, separating in the first section, was discarded.

B. Alkaline Solution from Ether-Chloroform Extract.—More than half the original chloroform-ether extract was removed by caustic potash, the solution having a deep red color. It was neutralized, the precipitate filtered, washed, and dried. It is quite soluble in sodium carbonate and in alcohol, and it is completely taken up by a sufficient quantity of ether. The substance is amorphous and is a resin. All attempts to isolate a crystalline body were fruitless.

---

[1] The solvent from the above, on concentration, deposits a small quantity of crystals (melting at 80°, softening at 50°). These were proved to be identical with the preceding substance.

[2] The ether extract of the acidified solution gave a small quantity of the fatty acid.

That the substances described above are not decomposition-products, produced by the action of the alkali during extraction, is shown by the fact that all were identified in the ligroin solution.

Ligroin Extract.—The ground bark was thoroughly exhausted with low-boiling ligroin (distilling on a water-bath), the solvent evaporated on a water-bath, and finally completely removed under diminished pressure. The residue was then dissolved in ether and the resulting solution allowed to evaporate slowly in the air. Crystals of the yellow body, melting at 216°, formed throughout the liquid, while at the bottom, a light-colored deposit formed. After a time the mother-liquor was decanted and the sediment washed with several small portions of ether, by which means it was possible to remove nearly all of the yellow substance. The residue, when pure, consists of a body which melts at 159°, and a small portion of the solid previously described as melting at 201°. On further standing, the ethereal solution deposited further quantities of the mixture, the amount of the substance melting at 201° steadily increasing. The two substances were separated by means of benzene, the substance melting at 201° being only sparingly taken up by this solvent, while that fusing at 159° dissolves quite readily.

The ethereal solution, after decantation, yields the substance mentioned above, melting at 50° to 80°, as a precipitate, when it is mixed with ligroin.

The ligroin extract therefore yields all of the neutral substances found in the chloroform with one addition. The detailed description of the various substances which were isolated follows:

Substance $C_{23}H_{20}O_7$ *; Melting-point 201°.*

The crude substance was purified by recrystallizing it from alcohol. By allowing it to separate slowly, it is obtained in highly refractive rectangular prisms, some of which have wedge-shaped ends. It is very soluble in chloroform, moderately so in benzene and acetic acid, sparingly in alcohol, and practically insoluble in ether and ligroin. It is insoluble in alkali.

I. 0.2428 gram substance gave 0.6015 gram CO_2; and 0.1092 gram H_2O.

II. 0.2734 gram substance gave 0.6779 gram CO_2; and 0.1278 gram H_2O.

	Calculated for $C_{23}H_{20}O_7$.	Found. I.	Found. II.
C	67.65	67.56	67.62
H	4.90	4.99	5.19

A molecular weight determination in naphthalene gave:

Solvent. Grams.	Substance. Gram.	Δ.	M.	Calculated molecular weight.
18.838	0.1923	0.175	409	408
"	0.4679	0.440	399	

From these and later considerations, the formula is shown to be $C_{23}H_{20}O_7$. The substance is decomposed by methyl alcoholic potash, two different crystalline products being obtained under different conditions.

1. Five grams of the body were boiled in a flask connected with a reflux condenser with 10 grams caustic potash in 500 cc. methyl alcohol for ten to twelve hours. The solution was then neutralized with hydrochloric acid, the alcohol nearly distilled off, the whole then acidified and precipitated with water, the precipitate filtered, washed, dried, and dissolved in a mixture of chloroform and ether, the latter then being extracted with a solution of caustic potash. This, when acidified, yielded a precipitate which, after being washed and dried, was recrystallized from alcohol, when it melted at 159°. The crystals consist of square, yellow plates, which are soluble in alcohol and chloroform, sparingly so in ether and benzene. The substance dissolves in a warm solution of sodium carbonate, but is precipitated on cooling. The yield was only about 35 per cent, the rest being recovered in unchanged condition. An analysis of a pure sample dried at 105° gave:

I. 0.1855 gram substance gave 0.4356 gram CO_2; and 0.0785 gram H_2O.

II. 0.2487 gram substance gave 0.5852 gram CO_2; and 0.1040 gram H_2O.

III. 0.1558 gram substance gave 0.3659 gram CO_2; and 0.0700 gram H_2O.

	Calculated.	Found.		
		I.	II.	III.
C	64.08	64.04	64.17	64.05
H	4.85	4.85	4.65	4.99

A molecular weight determination, which will be given below, makes the formula $C_{22}H_{20}O_8$ appear probable.

The substance takes up bromine readily.

2. Five grams of the compound $C_{23}H_{20}O_7$ was boiled in a flask connected with a reflux condenser with 7 grams caustic potash in 100 cc. methyl alcohol for three hours. The solution was then neutralized, the alcohol distilled off, and the whole acidified and precipitated with water. The precipitate, after being washed and dried, was dissolved in chloroform-ether and extracted with caustic potash. The chloroform-ether solution, on evaporation, yielded a crystalline product which was purified by recrystallizing from alcohol. It separates in very flat plates, having irregular edges (melting-point 136°). Soluble in chloroform, moderately so in alcohol and benzene, and slightly in ether. It is insoluble in caustic potash. It does not take up bromine as does the substance melting at 159°. An attempt was made to convert the substance melting at 159° into this by boiling with the stronger potash solution, but none could be obtained. The pure substance dried at 105° was analyzed with the following results:

I. 0.1666 gram substance gave 0.4073 gram CO_2; and 0.0778 gram H_2O.

II. 0.1646 gram substance gave 0.4001 gram CO_2; and 0.0866 gram H_2O.

	Calculated for $C_{22}H_{20}O_7$.	Found.	
		I.	II.
C	66.66	66.68	66.46
H	5.05	5.19	5.43

A series of molecular weight determinations of the following substances was made in ethylene dibromide:

1. Triphenylmethane; 2. Substance, $C_{23}H_{20}O_7$, melting at 201°; 3. Substance, $C_{22}H_{20}O_8$, melting at 159°; 4. Substance, $C_{22}H_{20}O_7$, melting at 136°.

	Solvent.	Substance.	Δ.	M found.	M (calc.).
I.	26.195	0.1294	0.245	238	244
		0.2747	0.520	238	
II.	23.910	0.1351	0.159	419	408
		0.2491	0.291	423	
III.	27.235	0.2330	0.231	437	412
		0.4127	0.401	446	
IV.	22.885	0.1438	0.178	416	396
		0.2829	0.355	419	

Action of Hydriodic Acid on the Compound $C_{23}H_{20}O_7$.

The substance in question is readily decomposed by hydriodic acid. A determination of methoxy groups was made according to Zeisel's method:

0.3103 gram substance gave 0.3593 gram of silver iodide.

Calculated for two methoxy groups, 0.3566 gram.

The structure, so far as the above experiments go, is therefore represented by $C_{21}H_{16}O_5(OCH_3)_2$.

The substance, in dry chloroform solution, instantly absorbs bromine, and, on evaporation, a crystalline residue can be obtained which is soluble in acetic acid. It melts at 152° to 154° with evolution of hydrobromic acid. It is not affected by alcoholic hydrochloric acid nor by the aqueous acid in sealed tubes at 130°. It does not color ferric chloride solution and is not precipitated by basic lead acetate.

What the relationship is between the compound $C_{23}H_{20}O_7$ and the two compounds produced from it by alcoholic potash, cannot be stated at present; both substances differ from the original only by loss of one carbon atom, and the substance $C_{22}H_{20}O_8$ has also gained oxygen. The quantity of substance obtainable even from a large amount of extract is too small to permit investigation of the products of deep-seated decomposition, so that the future must decide as to the constitution of these interesting compounds, when opportunity comes for obtaining large quantities.

Compound $C_{22}H_{18}O_6$, *Melting at 216°.*

The crude substance is purified by repeated crystallization from alcohol. It is obtained in beautiful, fine, yellow needles which dissolve in benzene and chloroform, sparingly in ether and alcohol, and are insoluble in ligroin, insoluble in water or alkaline solution. An analysis of the pure body, dried at 110° gave the following results :

I. 0.1688 gram substance gave 0.4321 gram CO_2 ; and 0.0751 gram H_2O.

II. 0.1698 gram substance gave 0.4361 gram CO_2 ; and 0.0746 gram H_2O.

	Calculated for $C_{22}H_{18}O_6$.	Found.	
		I.	II.
C	69.84	69.81	70.05
H	4.76	4.94	4.88

A molecular weight determination was made in naphthalene :

0.1673 gram substance gave Δ 0.227 gram in 14.73 grams solvent.

0.3935 gram substance gave Δ 0.507 gram in 14.73 grams solvent.

1. $M = 350$; 2. $M = 368$.

Calculated for $C_{22}H_{18}O_6$: $M = 378$.

The compound contains two methoxy groups :

0.2816 gram substance gave 0.3536 gram silver iodide.

Calculated for two methoxy groups, 0.3492 gram silver iodide.

The substance therefore has the formula $C_{20}H_{12}O_4(OCH_3)_2$.

In solution in dry chloroform it is slowly affected by bromine, hydrobromic acid being evolved ; in moist chloroform bromine is immediately taken up. On adding as much bromine as will be absorbed and then evaporating in a vacuum, a crystalline residue, which can best be recrystallized from benzene, is obtained. It melts at 267° with evolution of hydrobromic acid. The crystals are intensely yellow needles, very soluble in alcohol and ether, sparingly so in alcohol and benzene.

The analysis of this compound shows that it has two bromine atoms in the molecule, but, as, at the same time, a deep-seated change had apparently taken place, the figures do not allow us to express an opinion as to its nature.

The figures obtained for the substance $C_{22}H_{18}O_6$ are very close to those found by Hart for the so-called piscidine,[1] *i. e.*:

C, 69.78; 69.76; 69.69. H, 4.98 per cent.

Undoubtedly, the substance described as piscidine consists of a mixture of our two substances melting at 216° and 201°, as the melting-point was 192°.

In order to settle this question beyond doubt, we repeated Hart's process, with the result that we obtained the expected mixture, the substance melting at 201° being in large excess. Both substances were identified, after having been separated by the process described above, and as the crystals are very characteristic, there can be no doubt that piscidine really has no existence. Hart's carbon determinations are a little low, a natural result if he had a small amount of the substance melting at 201° in his mixture. Hart assigned the formula $C_{29}H_{24}O_8$ to piscidine. This substance was designated as the active principle of Jamaica dogwood, an assumption for which there is no foundation in fact, as a pharmacological investigation, undertaken by the kindness of Dr. Cushny, demonstrated.

Substance Melting at 50° to 80°.

The crude substance is very soluble in all of the ordinary solvents excepting ligroin, which takes it up only in small quantities. It could not be obtained in a perfectly pure state. When heated with slightly acidified alcohol, it soon deposits crystals of the substance melting at 216°, described above, and the resulting liquid reduces Fehling's solution readily. No other decomposition-product could be isolated, as the alcohol deposited a tar on evaporation. Five grams of the original substance yielded 2.5 grams of the body melting at 216°, after boiling for from five to six hours.

In solution in carbon tetrachloride, the substance decolorizes bromine instantly, with precipitation of the resulting product. This brominated body is insoluble in all ordinary solvents, but it can be purified by recrystallization from amyl alcohol. It melts at 245°. An analysis of this substance probably would clear up the relationship between the substance melting at 50° to 80° and that melting at 216°. Unfortunately, the quantity at our disposal was too small to admit of this investigation. It is probably a glucoside.

---

[1] This JOURNAL, 5, 9.

Substance Melting at 159° $(C_{25}H_{22}O_7?)$.

The body was purified by repeated crystallization from alcohol. Occurring as it does, mixed with the other substances mentioned above, it is very difficult to obtain it in a perfectly pure state. It appears to be in monoclinic crystals, colorless, soluble in chloroform and benzene, sparingly in ether and ligroin; insoluble in aqueous acid or alkaline solution. In pure chloroform solution, it takes up bromine with the formation of a crystalline derivative. An analysis of the pure substance, dried at 105°, gave the following results:

0.1382 gram substance gave 0.3512 gram CO_2; and 0.0691 gram H_2O.

	Found. Per cent.
C	69.18
H	5.26

A molecular weight determination was made in ethylene dibromide.

	Solvent. Grams.	Substance.	Δ.	M.	Calculated for $C_{25}H_{22}O_7$. M.
I	21.6	0.2071	0.274	413	434
II	"	0.3812	0.512	407	

Both the formulas, $C_{18}H_{16}O_5$ and $C_{25}H_{22}O_7$, are in good agreement with the results of the analysis, but the molecular weight determination is in better accord with $C_{25}H_{22}O_7$. The analysis could not be repeated on account of a lack of substance.

Substance Melting at 150° to 155° $(C_{20}H_{22}O_7)$.

The crude material was first recrystallized from absolute and then from 70 per cent alcohol, when it formed small, needle-shaped, colorless crystals, melting at 150° to 155° with decomposition and evolution of a gas. The substance is very soluble in ethyl or methyl alcohol, moderately so in acetone, and is sparingly dissolved by ether, chloroform, benzene, or hot water. It is insoluble in ligroin. It is readily taken up by hot alkalies, either caustic or carbonates, and is then colored red. The alcoholic solution becomes brown on standing, the chloroform solution blue; and when an attempt was made to dry the crystals at 100° they darkened materially. The substance reduces Fehling's solution and ammoniacal silver nitrate. Dissolved in alcohol it even blackens neutral silver nitrate. The body gives a green color with ferric chloride and is neutral.

Crystals dried *in vacuo* over sulphuric acid gave the following analytical results:

I. 0.1585 gram substance gave 0.3731 gram CO_2; and 0.0859 gram H_2O.

II. 0.1722 gram substance gave 0.4040 gram CO_2; and 0.0897 gram H_2O.

III. 0.1786 gram substance gave 0.4209 gram CO_2; and 0.0952 gram H_2O.

	Calculated for $C_{20}H_{22}O_7$.	Found. I.	II.	III.
C	64.17	64.20	64.08	64.27
H	5.88	6.02	5.79	5.92

The sample used in the third analysis was different from the other two.

A molecular weight determination was made in phenol.

Solvent. Grams.	Substance.	Δ.	M.
16.956	0.347	0.62	231

The result would make a formula (1) $C_{11}H_{10}O_4$ ($C = 64.08$, $H = 4.85$) the more probable one, but from considerations to be advanced below, there can be no question that the one given above (2) is correct. The solvent therefore has a partial dissociating action on the solute. Two other formulas, *viz.*, (3) $C_{17}H_{18}O_6$ and (4) $C_{23}H_{26}O_8$, are also in close agreement with the analytical numbers, but these must also be abandoned for similar reasons.

Action of Acids on the Substance $C_{20}H_{22}O_7$.

When heated with slightly acidified alcohol the compound is decomposed, and a much less soluble substance is precipitated, the same effect being produced by strong sulphuric acid. The latter method gives the best results.

Two grams of the shbstance $C_{20}H_{22}O_7$ were dissolved in concentrated sulphuric acid (2 parts acid to 1 part water) at about 50°. Solution immediately took place, a greenish-yellow color appeared and the temperature of the mixture rose. No odor was emitted, and no gas given off. The solution was then precipitated with water, filtered, and washed with water and dried (weight 1.8 grams). The crude substance was then recrystallized from glacial acetic acid and finally from alcohol.

The pure crystals are colorless and appear in the form of rectangular plates, melting at 275°, with slight coloration. They are moderately soluble in acetone, sparingly so in acetic acid, and almost insoluble in ethyl or methyl alcohol, ether, benzene, or chloroform. They are readily taken up by caustic potash or sodium carbonate on warming. They do not reduce either Fehling's solution or ammoniacal silver nitrate, even on warming, and they color alcoholic ferric chloride green.

I. 0.1512 gram substance gave 0.3643 gram CO_2; and 0.0699 gram H_2O.

II. 0.1375 gram substance gave 0.3329 gram CO_2; and 0.0655 gram H_2O.

III. 0.1569 gram substance gave 0.3811 gram CO_2; and 0.0762 gram H_2O.

IV. 0.1537 gram substance gave 0.3713 gram CO_2; and 0.0743 gram H_2O.

	Found.			
	I.	II.	III.	IV.
C	65.71	66.02	66.24	65.88
H	5.19	5.37	5.39	5.37

Calculated for I. $C_{18}H_{16}O_6$: C, 65.85 ; H, 4.88 ; M, 328.
II. $C_{21}H_{20}O_7$: C, 65.63 ; H, 5.21 ; M, 384.
III. $C_{15}H_{14}O_5$: C, 65.69 ; H, 5.11 ; M, 274.

A molecular weight determination in phenol gave :

Solvent.	Substance.	Δ.	M.
14.543	0.2109	0.365	286

Formulas (1) and (2) result from formulas (3) and (4) (given above), respectively, by separation of alcohol.

$$C_{20}H_{22}O_7 = C_{18}H_{16}O_6 + C_2H_6O;$$
$$C_{23}H_{26}O_8 = C_{21}H_{20}O_7 + C_2H_6O.$$

The filtrate from the preparation of the substance melting at 275° was, therefore, subjected to fractional distillation in the hope of detecting the presence of alcohol. The first fraction which passed over was tested with iodine and alkali, and a decided iodoform reaction was obtained. It did not reduce ammoniacal silver nitrate. The molecular weight agrees best with $C_{15}H_{14}O_5$, but by reason of results obtained by acetylation, this is not possible, so that here also the phenol has a dissociating effect as a solvent.

Acetylation of the Compound $C_{20}H_{22}O_7$.

When treated in the usual way with sodium acetate and acetic anhydride, the body readily yields an acetyl derivative in colorless crystals, melting at 183°. The substance is boiled for several hours in connection with a reflux condenser with 10 parts of acetic anhydride and 3 parts of sodium acetate. After cooling and pouring into water, it solidifies. It is filtered, washed with water, and recrystallized from alcohol to which a little animal charcoal has been added. The yield is apparently quantitative, and the body is pure after the first recrystallization. The body dried at 105° gave the following numbers:

I. 0.1462 gram substance gave 0.3361 gram CO_2; and 0.0684 gram H_2O.

II. 0.2112 gram substance gave 0.4872 gram CO_2; and 0.1005 gram H_2O.

Calculated for triacetyl derivative, $C_{26}H_{28}O_{10}$: C, 62.4; H, 5.6.

Calculated for diacetyl derivative, $C_{24}H_{26}O_9$: C, 62.88; H, 5.68.

	Found.	
	I.	II.
C	62.70	62.91
H	5.19	5.28

A molecular weight determination made in benzene gave:

Solvent. Grams.	Substance.	Δ.	M.
11.275	0.1895	0.171	491
"	0.4112	0.358	509

Calculated for $C_{24}H_{26}O_9$: M = 458.

On treating this acetyl derivative with sulphuric acid (5 parts acid to 2 parts water) it is dissolved on warming, and acetic acid is liberated. After heating in this way for two hours the product was diluted with water and a precipitate which formed filtered. This substance proved to be the decomposition-product, melting at 275°, described above, so that sulphuric acid splits off alcohol as well as acetic acid. As the compound melting at 275° is quite stable in the presence of sulphuric acid, an attempt was made to determine the number of acetyl groups present in the acetylation-products in this way.

0.5009 gram substance was dissolved in 12 grams of sulphuric acid (5 parts acid to 1 part water), and after heating on the water-bath for one hour was precipitated with 150 grams of water, then digested on a water-bath for a few minutes, allowed to cool, the residue filtered, washed, and weighed. Total, 0.3407 gram. The solubility of the same quantity of pure substance in the same amount of solvent is 2.9 per cent. Applying this correction, we have 0.351 gram, or 70.71 per cent of the original substance.

Calculated for $C_{18}H_{16}O_6$ from $C_{24}H_{26}O_9$ = 71.6 per cent.

A second experiment gave 69.5 per cent.

While this method is not suitable for exact quantitative work, it is nevertheless sufficiently accurate to show conclusively that the body is a diacetyl derivative.

Acetylation of the Substance Melting at 275° ($C_{18}H_{16}O_6$).

When treated in the same way as the compound melting at 150° to 155°, an acetyl derivative, separating from alcohol in crystals resembling calcite, melting at 177° to 178°, when in the pure state, is obtained.

I. 0.2184 gram substance gave 0.5089 gram CO_2; and 0.1025 gram H_2O.

II. 0.1660 gram substance gave 0.3899 gram CO_2; and 0.0755 gram H_2O.

III. 0.1518 gram substance gave 0.3560 gram CO_2; and 0.0717 gram H_2O.

	Found.		
	I.	II.	III.
C	63.55	64.06	63.96
H	5.21	5.19	5.25

A molecular weight determination was made in benzene :

Solvent. Grams.	Substance.	Δ.	M.
11.58	0.1488	0.149	419
"	0.3022	0.280	466

Calculated for $C_{22}H_{20}O_8$ (diacetyl derivative) : C, 64.08 ; H, 4.85 ; M, 412.

This substance is therefore a diacetyl derivative of the compound $C_{18}H_{16}O_6$, so that the separation of alcohol from the compound $C_{20}H_{22}O_7$ has not produced an additional alcoholic hydroxyl group.

The acetyl derivative dissolves in dilute sulphuric acid (2 parts acid to 5 parts water) with liberation of acetic acid. In this case, however, the sulphuric acid caused a certain amount of decomposition, so that an attempt to determine the number of acetyl groups as in the previous case resulted in numbers which fell between those calculated for two and for three groups, although nearer to the former. The precipitated body could not be obtained in a crystalline state.

Other Reactions of the Compound $C_{20}H_{22}O_7$.

The substance is quite readily decomposed by caustic potash and by means of a mixture of this and methyl iodide, a new body could be obtained.

The compound $C_{20}H_{22}O_7$ was dissolved in a small amount of a solution of caustic potash and then boiled on the water-bath with an excess of methyl iodide in methyl alcohol, small pieces of potash being added from time to time as the substance became neutral. The solvent was then evaporated, and the alkaline solution extracted with ether. On evaporating the ether, there remained a crystalline body, separating from methyl or dilute ethyl alcohol in needles, insoluble in petroleum ether ; melting-point 141° to 142°. Only enough substance remained for two analyses, which did not agree closely, but the numbers come closest to those calculated for a dimethyl derivative of the substance $C_{18}H_{16}O_6$ (melting-point 275°).

(Calculated : carbon, 67.41, hydrogen 5.6 ; Found : carbon 67.90, hydrogen 6.47).

The formula given for $C_{20}H_{22}O_7$ and its derivatives must be regarded as the most probable, but other series may be shown to agree with the results tolerably well. The molecular weight determinations were all more or less unsatisfactory owing to the high numbers, the acetyl derivatives did not yield entirely reliable results, and combustions of substances with such high molecular weights of necessity allow more than one interpretation, so the final disposition of the problem must be left for a time when, with larger quantities of material, sufficiently large amounts of methyl derivatives can be obtained to settle the question by a quantitative estimation of methoxy groups.

The bodies obtained from Jamaica dogwood, and so far as we know, the only ones present in this substance, are given in the following table :

Substance.	Formula.	Melting-point.
Piscidic acid	$C_{11}H_{12}O_7$	185°
Ethyl ester	$C_{13}H_{16}O_7$	207°
Anilide	$C_{23}H_{22}N_2O_5$	196°
Acetyl derivative	$C_{17}H_{20}O_9$	149°
Bromine "	$C_{11}H_{12}O_7Br_2(?)$	234°
Neutral solution.		
First body	$C_{23}H_{20}O_7$	201°, contains 2 methoxy groups
Decomposition-product of above	$C_{22}H_{20}O_8$	159°
Decomposition-product of above	$C_{22}H_{20}O_7$	136°
Second body	$C_{22}H_{18}O_6$	216°, contains two methoxy groups
Third "		50° to 80°
Fourth "	$C_{25}H_{22}O_7(?)$	159°
Fifth "	$C_{20}H_{22}O_7$	150° to 155°
Decomposition-product	$C_{18}H_{16}O_6$	275°
Acetyl derivative	$C_{24}H_{20}O_9$	183°
Acetyl derivative of 275° body	$C_{22}H_{20}O_8$	177°
Methyl iodide derivative	$C_{20}H_{20}O_6(?)$	141°

The present work has demonstrated the large number of interesting crystalline derivatives to be found in Jamaica dogwood, and it has given means for their isolation, together with some facts which show the direction which investigation must take in determining the constitution of the substances in question.

Scarcely any plant product shows so great a diversity of bodies, and a series, the members of which evidently are so closely related: The subject of the constitution of these bodies and their interrelationship will, in the future, form a most interesting chapter in plant chemistry. The investigation will have to be carried on with large quantities of the bark, not less than 400 or 500 pounds. At present the work must stand as it is, but we soon hope to be able again to take up the investigation of the structure of piscidic acid, of which larger quantities than of the other derivatives can be obtained.

ANN ARBOR, October, 1900.

THE CRYSTALLIZATION OF COPPER SULPHATE.

BY ARTHUR JOHN HOPKINS.

The Size of Crystals.

The work described in this paper had for its object the preparation of crystals of copper sulphate, which should be from 20 to 30 mm. in length. The first part contains a short discussion of those general conditions which determine the size of crystals, together with a development of a method for the preparation of crystals of any desired size. The following principles guided the work :

I. In the process of crystallizing copper sulphate, at constant room temperature, the solubility is a constant and the concentration (weight of solute in unit volume) minus this constant is the total weight of crystal deposit. Or, in other words, in the process of crystallizing copper sulphate at constant room temperature, the concentration determines the weight of the crystal deposit.

II. (*a*) In a solution, supersaturated in absolute quiet, no crystals will form.

(*b*) In a solution supersaturated in absolute quiet, the number of crystal points formed by the first disturbance (if the disturbance is succeeded by quiet) is the same as the number of crystals finally formed.

(*c*) The ratio between the number of crystals formed and the weight of crystal deposit determines the size of the crystals.

III. For a given volume of solution and given size of crystals and weight of crystal deposit, the diameter of the crystallizing dish determines the space between the crystals.

The usual laboratory practice of preparing a solution of known concentration with the expectation of getting crystals of definite size is therefore misleading, as this method gives only one definite result, *i. e.*, a certain weight of crystal deposit, as is expressed by the first principle. From principle II. it is clear that the number of crystals to be formed is determined almost instantaneously, *i. e.*, that nothing in the previous history of the solution (its concentration, the size of the dish, or the rate of cooling) directly determines the number of crystals, but that as the solution cools beyond the point of saturation, a few crystal points suddenly started, whether by direction or accidentally, will slowly grow by addition from the solution and, if given equal opportunity, will grow equally, each crystal's final weight becoming the quotient of the total weight of crystals deposited, divided by the number of points started.

Again, from the third principle, it is evidently desirable that the dish be large enough to allow the crystals full room to grow without crowding.

The experiments of the two parts of this paper number about 60. The first experiments are passed over. They proved that neither concentration alone, nor the relation of the size of the dish to the volume of the solution nor the rapidity of cooling determines the size of the crystals. These facts were all proved later by two experiments, as follows: First, bring a solution of definite volume and concentration to supersaturation in absolute quiet and then, after disturbing, note the size of crystals formed. Second, after warming the crystals and the solution obtained as described, repeat the first experiment, when crystals of an entirely different size will probably be deposited. A single such experiment shows that the slightest accident, after saturation, may determine the size of crystals.

In all of this work, dust was excluded as rigorously as possible by careful filtering of solutions and scrupulous cleaning of crystallizing and other dishes. In order to prevent carbonate from forming and acting as centers of crystallization, recently boiled water was used at first, then water known to be free from carbonic acid, but finally it was found necessary (in continued crystallizations of the same solution) to add about 5 cc. of normal sulphuric acid to every 100 cc. of solution. Uniformity in measuring (without danger of error due to contraction on cooling to indefinite degrees) was approximated by concentrating the filtered and perfectly clear solution in a marked beaker to a volume smaller than that desired, pouring quickly into a hot measuring cylinder, transferring the last drops by aid of a little boiling water, filling the cylinder to the desired volume with boiling water, and pouring the solution quickly into a clean crystallizing dish, which was immediately covered. All of these experiments were conducted in a room held at constant temperature by a heat regulator, and a watch was kept on the indications of a maximum and minimum thermometer. A variation of 2° was unusual and occurred only during the night.

Experiments showed that solutions of convenient concentration and volume were obtained, when 171 grams of clean copper sulphate crystals were dissolved in water and 15 cc. of normal sulphuric acid were added, and the whole was concentrated to less than 340 cc. and diluted to exactly that volume with boiling water, the volume being read when the solution was as near as possible at boiling temperature. All the solutions were started in this way, and all solutions, not of the same volume, were of this concentration. The size of the crystals decided upon as desirable for quantitative work was a length varying from 20 to 30 mm. The ratio of the volume of solution to the horizontal surface of the containing crystallizing dish is identical with the depth of solution, and so for each volume a dish was selected which would give a constant depth. A depth of about 6 mm. was found to give ample space between crystals 20 to 30 mm. long, formed from a solution of the strength indicated; and in so shallow a solution there is the added advantage that the crystals, when first formed on the surface, fall to the bottom directly without slant. The diameter of the dish, which will hold 340 cc. at a depth of 6.3 mm., is 26 cm., and, in general, the diameter for this depth is the square root of twice the contained volume.

From the previous discussion it will be seen that with a given volume and concentration and with the size of the dish determined, the size of the crystals will depend upon the number of crystal points first started in the solution as it cools beyond the point of saturation, and that the number of these points depends upon the conditions which obtain in the crystallizing dish during the time of supersaturation, and only then. Of course one can escape the uncertainty of accident by providing in such a solution a sufficient number of minute, clean crystals to supply nuclei for crystallization, but these should be so small as not materially to increase the concentration. A difficulty would arise in this method of procedure in that the temperature would have to be chosen so low that the little crystals would not dissolve in the hot solution before growth began, and also so high that the cold crystals would not locally chill the surface of the solution below the saturation-point and thus start crystallization in a fine powder throughout the whole mass. For the volume and concentration above indicated, about fifty such points would be necessary to give crystals of 30 mm. in length.

The method used in this work for starting the proper number of crystal points is one which, with a little practice on the part of the experimenter, works satisfactorily—how much so will be seen from the second part of this paper. When the hot measured solution is poured into the crystallizing dish, the latter is carefully covered to prevent further concentration, dust or surface chilling, and is allowed from eight to ten minutes to cool, when a slight blast of air (the air being filtered through cotton) under pressure equivalent to 12 mm. of mercury is blown upon the surface, and the latter is watched closely for the first minute crystals which (formed before the colder blast) float out upon the surface. When the proper number of these crystals for the volume and concentration are not only formed but persist in the hot solution, the blast is quickly removed, and the crystals are allowed to grow while the dish is covered and left undisturbed at constant temperature, usually over night. As the number of crystals always bears the same relation to the surface exposed, one watches not for a certain number of crystals but rather for a certain spacing, constant for each experiment, which it is easy to approximate each time.

Successive Crystallizations.

In the experiments mentioned above, 171 grams of clean copper sulphate crystals were dissolved in acidified water and concentrated to 340 cc. On crystallization at 23° (C.), 275 cc. of mother-liquor and 78 grams of crystals were obtained. It was desired to evaporate further the 275 cc. of concentrated solution to the same strength as the 340 cc. of the original solution—a concentration which will always give the ratio of 78 grams of crystals to 275 cc. of mother-liquor. It was calculated[1] that to this end any saturated solution of copper sulphate must be evaporated to 67.1 per cent of its volume, and that this will then give a mother-liquor equal to 54.3 per cent and a crystal weight equal to 15.4 per cent of the same volume.

Based upon this calculation, a model has been constructed which is found in Table I., below. According to this table, each mother-liquor is to be concentrated to 67.1 per cent of its volume, and from it is to be obtained a weight of crystals and a volume of new mother-liquor in the ratio of 28+ grams to 100 cc. Table II. contains the results of the first attempt to follow this model. By comparing these tables, it will be seen that the point of concentration indicated in the second column of Table I. was not reached exactly in any case but the important column VI. of Table II. shows that the size of crystals has fallen each time within the desired limits of from 20 to 30 mm. in length.

---

[1] The calculation is as follows:

$$275 : 78 = 100 : 28.3.$$

Solubility at 23° = 21.7 grams $CuSO_4$, sp. gr. of solution being 1.21+.

$$21.7 \text{ grams } CuSO_4 = 33.8 \text{ grams } CuSO_4.5H_2O.$$

Required: $0.338\ V - 0.338\ V' = 0.283\ V'$, or mother-liquor, V', = 54.3 per cent V.

Then the original solution at point of saturation at 23° must have measured $275 \div 0.543 = 506.4$ cc.

$340 \div 506.4 = 67.1$ per cent, evaporating ratio.

$0.284 \times 0.543 = 15.4$ per cent, ratio of crystal weight to saturated solution.

Table I. Model.

Process number.	I. Solution saturated at 23°. Each volume = 54.3 per cent of preceding. cc.	II. Solution evaporated to 67.1 per cent of volume in I. cc.	III. Weight of crystals = 15.4 per cent of volume in I.	IV. Ratio of weight of crystals to volume in I.	V. Diameter of crystallizing dish to give solution in II. a depth of 6+ mm. $D = \sqrt{2.V.}$	VI. Size of crystals.
1	[506.4 calculated]	340			$\sqrt{680} =$ 26	
	275		78	0.283		
2	275	184			$\sqrt{369} =$ 19	
	149		42	0.282		
3	149	100			$\sqrt{200} =$ 14	
	81		23	0.284		
4	81	54			$\sqrt{109} =$ 10.5	
	44		12.5	0.284		

Table II.

	I.	II.	III.	IV.	V.	VI.
1	x	340			25	20
	275		78	0.283		
2	275	190			20	20
	157		39	0.248		
3	157	105			13.5	26
	85		25	0.294		
4	85	58			9.6	26
	50		12+	0.24		

It should be said concerning the figures in columns I. to IV. that it is very difficult to measure quickly solutions which are held as closely as possible to the boiling temperature, and that an approximation to the model was all that was necessary, since large variations do not appreciably affect the results in column VI., which contains the results especially sought.

When the solution gets as small as 58 cc., the nuclei may be supplied by introducing minute crystals—as only ten are needed in this case—but these crystals must first be washed with hot water and must then be large enough to exist in the hot solution. In larger solutions the method described is better.

Should one desire to form crystals of a different size, a little practice would be necessary to determine the proper condition of spacing for that size, and the formula for the size of the crystallizing dish would be somewhat changed. It would then be possible to prepare crystals of any desired size not only from the original solution but from all the successive mother-liquors.

AMHERST COLLEGE, September, 1900.

ON METHYL CYANIDE AS A CATALYTIC REAGENT; AND A CRITICISM OF J. U. NEF'S VIEWS ON THE FRANKLAND, WURTZ, AND CONRAD REACTIONS.

BY ARTHUR MICHAEL.

In the Wurtz sodium method for preparing alkanes it has been found necessary, in some cases, to heat the ingredients in a closed tube; an operation that not alone greatly increases the difficulty of preparation, but also, usually, materially decreases the yield of hydrocarbon obtained. Several chemicals, like ether and acetic ester, have been found to facilitate the reaction with certain iodides, but I have failed to notice any decided influence in some other instances, which have come under my notice. A number of other organic substances were examined, and in methyl cyanide the catalytic property was noticed to be developed to a very considerable degree. I- was intended to investigate this interesting subject more caret fully, but as several years have already passed and I have been unable to do so on account of other more pressing work, these incomplete observations are communicated, in the hope that this new catalytic reagent may prove of service to chemists who are now working in this field.

The behavior of methyl iodide towards sodium was examined by Buckeisen and Wanklyn,[1] who heated these substances and ether in a sealed tube to 100° and obtained ethane, mixed, however, with methane in considerably larger proportion, and a small amount of ethylene. Sodium wire does not react with dry methyl iodide, even after standing some hours at room temperature, but if the mixture is well cooled in ice-water, and a drop or two of methyl cyanide added, an energetic reaction soon takes place, with formation of a permanent gas that, to judge from the color of its flame, could have hardly contained an appreciable proportion of ethylene.

---

[1] Ann. Chem. (Liebig), **116**, 329.

The behavior of ethyl iodide towards sodium has not been examined, although Löwig[1] has described the formation of normal butane by the action of sodium amalgam. Sodium wire and ethyl iodide react very slowly and imperfectly at ordinary temperature, but the addition of a drop or two of acetonitrile soon causes, according to the dilution of the cyanide, a reaction, which, if not moderated by cooling, may become very violent. To prepare butane by this method it is advisable to connect the lateral tube of a fractionating flask with a condenser and its neck with a dropping-funnel, and, after introducing the sodium wire and some dry ethyl iodide into the flask, to displace the air by a current of carbon dioxide. Several drops of acetonitrile are then added, and the reaction kept in moderation by sufficient cooling, adding from time to time more iodide, which may contain a very small amount of the nitrile. A good yield of butane is obtained in this way, which may contain some ethane and ethylene, but, if present at all, they certainly are in much smaller proportion than when butane is prepared by the Frankland method.

Normal hexane was prepared by Schorlemmer,[2] who found that sodium does not react on propyl iodide in presence of ether, even on boiling the mixture, and obtained the hydrocarbon by heating the iodide and metal in a sealed tube to 150°. If several drops of acetonitrile[3] are added to sodium wire, covered by propyl iodide, a reaction is immediately noticeable, and, if the dilution is not very great, the mixture soon begins to boil, and cooling becomes necessary; thus, two drops of the nitrile added to 10 grams propyl iodide and the equivalent amount of sodium, caused a violent reaction in a few minutes, while at five times this dilution the reaction proceeds gently, under slight warming, and continues for about twelve hours; in either case a small quantity of iodide remained unconverted. In an experiment with 310 grams of propyl iodide, with 10 per cent excess of sodium wire, in a flask connected with a return condenser, 5 drops of cyanide were added, and the mixture allowed to stand for a day. Then it was heated on a water-bath for several hours, and the hydrocarbon distilled off. The hexane thus obtained was heated to 100° in a sealed tube, with a little sodium, for eight hours, and, after fractionation, was found to be pure. The yield was 80 per cent of the theory, which probably could have been somewhat increased by very careful handling of this volatile hydrocarbon.[1]

---

[1] J. prakt. Chem., 79, 441.

[2] Ann. Chem. (Liebig), 161, 277.

[3] According to Stohman and Kleber (J. prakt. Chem., [2], 43, 7) freshly pressed sodium wire reacts at once on propyl iodide, but, although this experiment was repeated several times, we never noticed a reaction until the nitrile was added.

The following experiments should be considered as preliminary tests:

Allyl iodide and sodium, according to Berthelot and Luca,[2] react on heating to form diallyl, but it is not necessary to heat the mixture, although at room temperature the reaction proceeds very slowly. Addition of several drops of acetonitrile soon induces a violent reaction, which it is well to moderate by cooling in ice-water, with formation of diallyl, apparently with a good yield.

Isopropyl iodide and sodium wire did not react, but on addition of a little nitrile, a decomposition occurred after the mixture had stood about half an hour.

Trimethylene bromide was only very slowly decomposed by sodium, which at first was not increased by addition of the nitrile, but after about twenty minutes a rapid reaction took place, with evolution of gas.

Benzyl chloride reacts slowly with sodium wire at ordinary temperature, and the preparation of dibenzyl is effected by heating the mixture.[3] Addition of acetonitrile soon induces a reaction, which proceeds rapidly, unless the mixture is cooled. The yield of dibenzyl, according to this method, is greater than when sodium is used alone at a higher temperature, as less by-products are formed.

This catalytic property of methyl cyanide is shared by ethyl and propyl cyanides, although, particularly in the case of the last substance, the inductive capacity appears to be less developed, and with aromatic cyanides, benzonitrile and benzyl cyanide, no acceleration of the reaction was noticed. It would seem that these conditions indicate an influence of the fatty cyanides, which is not dependent on the action of the metal on them, as benzonitrile, which does not act as an inducer, is also attacked by sodium.

---

[1] The experiments with propyl iodide were done with W. W. Garner.

[2] Ann. chim. phys., [3], 48, 294.

[3] Ann. Chem. (Liebig), **121**, 250; *Ibid.*, **137**, 258.

In connection with a research on the action of zinc ethyl iodide and zinc ethyl on unsaturated α,β-esters[1] several experiments were made, which gave results connected with the inducing properties of esters on the action of zinc on ethyl iodide, and these will be mentioned in this note.

It is a well known fact that ethyl iodide reacts but slowly on zinc, even when heated with it, and that the formation of zinc ethyl iodide may be greatly facilitated by the addition of ether or acetic ester. The following experiment indicates that oxalic ester can also act as an inducer. Ten grams of dry ethylene bromide (dried over phosphorus pentoxide) and 5 grams freshly pulverized zinc-sodium were heated, first to 100°, then, as no action took place, to boiling; but even at that temperature only a very slight evolution of a gas was noticed. The mixture was then cooled and 8 grams of dry oxalic ester added, when, on heating to about 40° C., a vigorous evolution of a gas occurred, which burnt with an almost colorless flame. After the reaction moderated it was completed by heating the flask for some hours to 100°, which was then heated, connected with an inverted condenser, in a salt-water bath as long as an oil passed over. In this way 3 grams of oil were obtained, which boiled almost entirely at 39°, and consisted of ethyl bromide :

0.1363 gram oil gave 0.2341 gram AgBr.

	Calculated for C_2H_5Br.	Found.
Br	73.3	73.1

The inducing influence of ether in the preparation of zinc ethyl was first noticed by Frankland, and later Pebal[2] based a method for obtaining that substance in an open vessel on this observation. If zinc and ethyl iodide, in equivalent proportions, in a flask connected with an inverted condenser, are mixed with an equal volume of dry ether, and, after driving out the air in the apparatus by carbon dioxide, are heated on a water-bath, the zinc is gradually used up, without evolution of gas in a considerable proportion. The ether contains a good yield of zinc ethyl iodide, which is left as large, white crystals when the solvent is driven off. It seems to have been overlooked that this substance may be used in many of the preparations, which involve the use of zinc ethyl, and the synthesis of ethylphenylketone is given as an example of the method. Twenty-five grams of ethyl iodide were converted into zinc ethyl iodide, the solution cooled in ice-water, and 22.5 grams benzoyl chloride, diluted with twice its volume of dry ether, gradually added. The reaction proceeded in the cold, and next morning all the chloride had disappeared. The contents of the flask were thrown on broken ice, then acidified thoroughly, shaken, and the ether separated and extracted with caustic soda. On fractionation of this ethereal solution about 30 per cent of ethylphenylketone was obtained, besides 4 grams of product boiling from 193°–196° under 9 mm. and a little of a white crystalline substance, neither of which bodies was further examined. A better yield of diethyl ketone was obtained by using this method, and it seems likely that, if the exact amount of zinc ethyl iodide formed from a given weight of ethyl iodide were ascertained, the process might advantageously replace that which involves the use of zinc ethyl in many synthetical reactions.

---

[1] Michael : Ber. d. chem. Ges., **29**, 1791 ; J. prakt. Chem. (N. F.), **60**, 477. The details of this work will be published later.

[2] Ann. Chem. (Liebig), **118**, 22.

The action of zinc on a mixture of ethyl iodide and malonic ester has been investigated by Daimler,[1] who found that, on warming the mixture, ethane is given off and ethyl malonic ester is formed. According to the interpretation of this interesting synthesis given by the discoverer, the metal probably works indirectly, first acting on the ethyl iodide. Daimler only mentioned this construction of the reaction, leaving the details and further procedure an open question, but the following experiments show that the reaction proceeds with the formation of zinc ethyl iodide, which, reacting with malonic ester, yields a metallic derivative, and that the further action of ethyl iodide on this product proceeds with formation of ethyl malonic ester and zinc iodide. Twenty-five grams of ethyl iodide were converted into zinc ethyl iodide, and 24.5 grams of malonic ester were slowly added to the ethereal solution, cooling, when necessary, to avoid a violent reaction. During the operation a gas came off abundantly, which burnt with a pale flame and evidently consisted of ethane. After standing twelve hours,[1] 24 grams of ethyl iodide were added, and the mixture boiled four hours. On adding the product to ice-water no gas was evolved, and the ether solution, after drying, gave, on fractionation, the following result :

---

[1] Ann. Chem. (Liebig), 249, 173.

		Grams.
I.	205° –208°.5	0.8
II.	208°.5–214°	18.0
III.	214° –217°	3.0

On refractionating II. and III. several times with beads, 12 grams of oil boiling from 209°.5 to 211°.5 were obtained, which consisted of pure ethyl malonic ester, and 8 grams oil boiling from 211°.5 to 217°, probably mostly ethyl—with some diethyl malonic ester. An analysis of the portion boiling from 209°.5-211°.5 gave the following result :

0.1582 gram of oil gave 0.3340 gram CO_2; and 0.1224 gram H_2O.

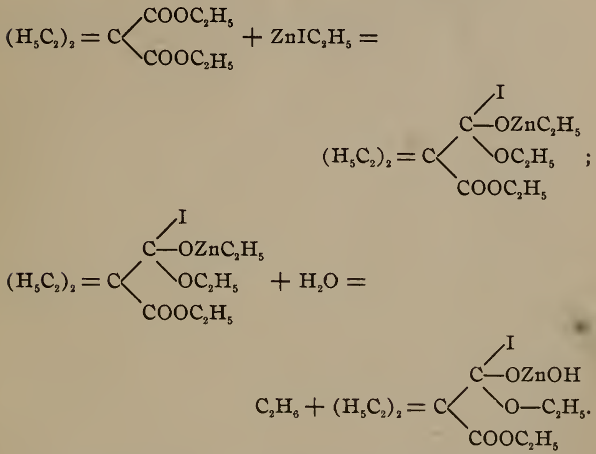
	Calculated for $C_9H_{16}O_4$.	Found.
C	57.4	57.6
H	8.5	8.6

Diethyl malonic ester acts, as a neutral body towards sodium, and the following experiment showing, not alone the inductive influence of the ester in forming zinc ethyl iodide, but also that it may form a metallic derivative, is not without theoretical interest. Five grams ester, 3.5 of zinc, and 8.3 of ethyl iodide were heated, under a pressure of 100 mm., for twelve hours, when almost all the zinc had disappeared. The evolution of gas during this operation was comparatively slight. The ethereal solution was thrown into

---

[1] If this product is thrown into acidulated water, malonic ester is regenerated.

250 cc. cold water, when considerable ethane was given off, the liquid well shaken, and the voluminous precipitate filtered under pressure, washed, and well pressed between filter-paper. This precipitate contained zinc and iodine, and after decomposition by an acid, gave 3.2 grams of an oil, which boiled from 223° to 228° (corr.), and consisted largely of unchanged diethyl malonic ester. A possible interpretation of this behavior may be represented by the following equations :



In a recent paper[1] J. U. Nef has treated the formation of ethyl malonic ester by means of zinc, as well as the Frankland, Wurtz, and Conrad syntheses, from a peculiar point of view. These conceptions of Nef's arise from an imperfect understanding of the fundamental chemical processes, particularly that of the relations of elimination and addition to chemical structure and to each other, and in misunderstanding[2] the conditions that lead to the formation and existence of divalent carbon. I have already shown[3] such a criticism of a portion of Nef's paper, to be well founded, and it is not difficult to prove that his interpretation of the Frankland, Wurtz, and Conrad reactions is open to the same objections. The idea that some reactions, which apparently have gone by substitution are, in reality, the result of an eliminative process, followed by that of an additive, inasmuch as the unsaturated body first formed passes over, by addition of one of the reagents used or of a substance formed in the reaction, into a saturated compound, is by no means as new as Nef supposes. It was discussed by Linnemann[1] in his papers on the direct conversion of certain primary propyl and isobutyl derivatives into corresponding secondary and tertiary products; and this explanation was considered by V. Meyer[2] as a satisfactory explanation for some of these abnormal reactions. Tscherniak[3] assumed that the appearance of nitrous esters in the action of ethyl iodide and its homologues on silver nitrite is due to the formation of alkylenes, which unite with the nitrous acid formed in the reaction; but later, Meyer[4] showed that propyl and isopropyl iodides give isomeric nitrites, whereas, if their formation were due to the intermediate formation of propylene, isopropyl nitrite alone should be generated. Linnemann[5] returned to this method of explanation, and, as he proved that propylene bromide with zinc and water at 100°, *i. e.*, nascent propylene, does not form isopropyl addition alcohol, he considered the addition hypothesis inadequate.[6]

---

[1] Ann. Chem. (Liebig), 298, 202.

[2] Michael : J. prakt. Chem. (N. F.), 60, 478.

[3] *Ibid.*, 60, 471.

The first experimental proof that elimination may precede substitution was given by the writer,[7] who showed that α,β-dibrompropionic ester and α-bromacrylic ester in their reaction with sodium malonic ester give the same product, an observation which led to the discovery of the property of α,β-unsaturated esters and ketones to give addition-products with such sodium derivatives.[8]

---

[1] Ann. Chem. (Liebig), **161**, 53; **162**, 29.

[2] Ber. d. chem. Ges., **9**, 529, 535; **10**, 130.

[3] Ann. Chem. (Liebig), **180**, 157.

[4] Ber. d. chem. Ges., **9**, 534.

[5] *Loc. cit.*, **10**, 1111.

[6] The conditions in these experiments and in those of nitrous acid on propylamine are not strictly comparable, as the presence of an acid materially facilitates the addition of water. However, there is as yet no proof that the formation of secondary propyl alcohol in the latter instance results from that of propylene.

[7] J. prakt. Chem., (2), **35**, 132.

[8] *Loc. cit.*, 349. It may be observed that the short account given above by no means represents the complete literature on this subject.

It was especially emphasized[1] at the time that, when elimination proceeds very easily, as is the case with α,β-dibrompropionic ester, and when under the observed conditions the unsaturated derivative thus formed can unite with the other reagent, it is absolutely necessary to take the possibility of the reaction going in this way into consideration. The experience of Bischoff[2] and Auwers and Jackson[3] several years later, in the study of the action of sodium malonic ester on α-bromisobutyric ester tended to confirm the necessity of determining the relations of eliminative and substitutive processes to chemical structure. In recent years, several other reactions bearing on this subject have been carefully studied, and I have been able to prove, step by step, that such eliminative and subsequent addition processes really occur, as well as to connect the relations between them and substitution with the chemical structure of the substance, so that we now know, in most cases, when we may expect one or the other decomposition, or a mixed reaction, resulting from a simultaneous procedure in both directions.[4]

It is interesting to note the changes in the elimination and addition theory that have been suggested by Nef, and for our purpose it will suffice to discuss the behavior of propyl iodide and isopropyl iodide to obtain a proper appreciation of his ideas. Nef[5] starts with the assumption that malonic ester is a perfectly neutral compound, an assumption that is based on some inaccurate observations of his own.[6] He then concludes that because sodium malonic ester is decomposed by water it must also undergo a like decomposition to a great extent by absolute alcohol; which represents such an obviously wrong assumption that it is not necessary to discuss it. The next step assumes the dissociation of the iodides by sodium ethylate into propylene and hydriodic acid, and that the free malonic ester present, or that formed by the acid reacting on sodium malonic ester, then adds to the nascent propylene to form propyl malonic ester. These assumptions complete the chain of impossible conceptions, for, not only can we perform the same reactions with sodium malonic ester that is free of malonic ester or alcohol, but sodium malonic ester, as was shown a number of years ago,[1] adds equally well to unsaturated α,β-esters in the absence as in the presence of alcohol. Moreover, according to Nef's views, propyl and isopropyl iodides and sodium malonic ester can give but one and the same product, which should be isopropyl malonic ester, for the addition of reagents whose additive parts consist of hydrogen and an atom or radical negative to that element, invariably leads to an isopropyl derivative. There is, perhaps, no better established fact in organic chemistry than that normal alkyl iodides and sodium malonic ester yield normal alkyl malonic esters, whereas isoalkyl iodides give isoalkyl malonic esters. Furthermore, it is a well known relation that secondary iodides lose hydriodic acid more easily than the primary, and that the tertiary derivatives do so more easily than the secondary; further that it is considerably more difficult to add reagents to alkylenes than to isoalkylenes. If, therefore, the speculations of Nef were permissible, the ease of replacement of sodium in sodium malonic ester should be in the order of tertiary, then secondary, and finally primary alkyl, whereas, even from the earliest investigation on this subject, that of J. Wislicenus, on the replacement of sodium in sodium acetacetic ester by alkyl, it is certain that the relative order of ease of substitution greatly decreases from primary to tertiary iodides; indeed, in this instance, it was found impossible to replace sodium by tertiary butyl.[3] Numerous investigations since then have only emphasized these relations, which in themselves so amply disprove the interpretations of Nef, that any further evidence of their impossibility, which it would be easy to adduce, does not seem necessary.

---

[1] *Loc. cit.*, 356.

[2] Ber. d. chem. Ges., **23**, 1464.

[3] *Loc. cit.*, 1599.

[4] Ber. d. chem. Ges., **28**, 2512; **29**, 1792. J. prakt. Chem., (N. F.), **60**, 372–384 409–420.

[5] Ann. Chem. (Liebig), **298**, 262.

[6] Ann. Chem. (Liebig), **266**, 67; Compare Michael: J. prakt. Chem., [2], **46**, 194; Conrad and Gast: Ber. d. chem. Ges., **31**, 1339; Willstätter: *Loc. cit.*, **32**, 1276.

In the above paper, Nef selected a considerable number of reactions which to him seem abnormal, and as he fails to understand the reason of their apparently abnormal behavior, he attributed a very mysterious dissociating property to many, comparatively inert, substances, which often, without any apparent reason except to make Nef's views seem less impossible, cause chemical changes involving a great expense of energy. Thus, in regard to the Daimler synthesis, he overlooks the suggestion of that chemist, that the first phase of the reaction consists in the formation of a zinc ethyl derivative, and after reiterating, what Daimler[1] had already emphasized, that the direct formation of zinc malonic ester is practically impossible under these conditions, Nef concludes that his views on the mechanism of this reaction are especially corroborated by Daimler's experiments. The experimental analysis of this reaction mentioned above, shows conclusively that not the slightest support for Nef's views is to be found in the synthesis in question.

---

[1] Michael and Schultheiss: J. prakt. Chem., [2], **45**, 55.

[2] Ann. Chem. (Liebig), **212**, 239.

[3] *Ibid.*, 244.

Nef's conceptions in regard to the Frankland and Wurtz syntheses are open to the same criticism. Beginning with methyl iodide, the ease of elimination of hydriodic acid increases in the primary alkyl iodides to at least the sixth series; when sodium acts on an iodide it exerts an attraction not only for iodine but also for hydriodic acid, and, if the conditions are such that the formation of hydriodic acid is favored, a correspondingly large proportion of the iodide will pass over into the respective alkylene, which may be more or less reduced by the nascent hydrogen formed by interaction of the acid with the metal used. This formation of alkylene must take place still more easily with secondary and tertiary iodides, in which compounds the capability of direct substitution is decreased, while that of the elimination of hydriodic acid is increased.[2] From this point of view all the facts enumerated by Nef, which he believes to be inexplicable by our present conceptions, are easily explained, and we certainly do not need to take refuge in an hypothesis, that assumes ethylene that will be reduced only to ethyl, because it and hydrogen are formed in the proportion of a molecule to an atom, or whose author[3] particularly emphasizes that, according to his own hypothesis, sodium in reacting on propyl iodide and isopropyl iodide should give the same hexane, although he should have been aware that isomeric hydrocarbons have actually been made in this way,[1] and that the physical properties of these two bodies have been carefully examined. The criticism of Nef's views may be left at this point, but it certainly does not seem unreasonable to expect from a chemist, who proposes to revolutionize the present theories, a more thorough knowledge of facts and a better acquaintance with these theories.

---

[1] Ann. Chem. (Liebig), 249, 174.

[2] Michael: J. prakt. Chem., 60, 368–384, 409–424.

[3] Ann. Chem. (Liebig), 298, 272.

Tufts College, Mass.

ON THE FORMATION OF PLATINUM TETRACHLORIDE FROM AQUEOUS HYDROCHLORIC ACID BY ATMOSPHERIC OXIDATION IN CONTACT WITH PLATINUM BLACK.

By J. W. Mallet.

A considerable quantity of platinum black was prepared from a solution of the tetrachloride, using as reducing agent the commercial solution of formic aldehyde (so-called "formalin") in the presence of sodium hydroxide at the boiling temperature.

The precipitated metal was filtered off, and washed at first with water. When most of the sodium chloride had been washed away the finely divided metal began, as usual, to come through the filter, rendering the filtrate black and turbid. Stopping the washing, the platinum on the filter was allowed to stand for several hours, and had become partially dried when it was attempted to renew the washing with a fairly strong aqueous solution of hydrochloric acid, in the hope that a clear filtrate might be better secured with this than with water alone. Almost immediately the liquid came through the filter clear, but of a deep sherry color, and was found to contain platinum in solution in abundance. Continuing the washing, the color diminished, and after a little while the filtrate was almost as colorless as before turbidity had first appeared in the aqueous washings.

I am not aware that the removal of hydrogen from hydrochloric acid by oxygen occluded from the air in platinum black has been before now observed and recorded.

---

[1] Schorlemmer: Ann. Chem. (Liebig), **144**, 184; **161**, 277; Bruehl: *Ibid.*, **200**, 184; Zander: *Ibid.*, **214**, 165; Schiff: *Ibid.*, **220**, 87.

NOTES.

Ammonium Amalgam.

Coehn[1] has recently published the results of an investigation on this subject, and these are given here in abstract. The increase in volume which takes place during the formation of ammonium amalgam has been used as an argument in favor of the view that ammonia and hydrogen are absorbed as such by the mercury, and that a distinct substance, ammonium, is not in combination with the mercury. In opposition to this view it has been shown that the volumes of the gases evolved bear to each other the ratio $NH_3 : H = 2 : 1$; and further, that neither ammonia nor hydrogen is absorbed by mercury.

An attempt has been made by Landolt to obtain some experimental evidence of the metallic nature of the substance ammonium, contained in the amalgam, by bringing the freshly prepared amalgam into solutions of salts of the heavy metals and determining whether, under these conditions, ammonium can replace these metals from their salts. Treated in this manner, neither copper, nor silver, nor iron, could be precipitated. This, he says, is opposed to the view that ammonium has a metallic nature.

Le Blanc thought it possible that the ammonium might be so unstable that it would not have the power to replace metals but would decompose into ammonia and hydrogen, as soon as liberated from the amalgam.

He attempted to solve the problem as to the nature of the substance contained in the amalgam by electrolyzing solutions of ammonium salts, using a mercury cathode, and comparing the polarization on the one hand with that which results when an alkali amalgam is formed in this way, and, on the other, with that which is obtained when hydrogen alone is developed on the cathode. If the value found approximates that obtained by electrolyzing an alkali salt it would argue in favor of the existence of ammonium in the amalgam. If, on the contrary, it approached the value when hydrogen alone is developed on the cathode, it would argue against the existence of ammonium. His results pointed to the existence of ammonium in the amalgam.

It has been shown that in addition to the tension at which the development of hydrogen takes place in a reversible manner, as in platinized platinum, there is a characteristic tension for each metal. Thus, the reversible evolution of hydrogen, obtained by discharge of hydrogen on a mercury cathode with continuous current, took place at 15.2 volts. If an alkali metal is in solution, using the mercury cathode, there is obtained in addition to the point at 15.2 volts another point beneath this, which changes with the nature of the alkali metal, and is, therefore, characteristic of the latter, and corresponds to the formation of the amalgam. This took place with ammonium at 1.24 volts, and is therefore completely analogous to the case of the alkali metals.

---

[1] Ztschr. anorg. Chem., 25, 430.

The only argument against the metallic nature of ammonium still remaining was that of Landolt, and it is this which Coehn has tested in a different manner and under different conditions. The ammonium amalgam was freshly prepared by electrolysis and dropped into a solution containing copper sulphate. A platinum wire which was connected through a galvanometer with a platinum plate suspended in the solution projected upward through the bottom of the vessel. The amalgam came in contact with the platinum point, and the action of the element, if copper is replaced, would be to deposit copper on the plate, with the simultaneous passage of a current through the galvanometer. It was found that no copper was deposited, and only a weak current of momentary duration passed through the galvanometer. To test whether Le Blanc was correct in supposing that ammonium was too unstable to replace other metals, he prepared the amalgam so that it would be more stable by electrolysis of ammonium salts, cooled down nearly to 0°.

It was found that the amalgam thus prepared did not show the tendency to swell up unless it was warmed, and it has quite a metallic appearance. When ammonium amalgam, thus prepared, was brought into a solution of copper sulphate, cooled to about the same temperature, the formation of copper amalgam could be seen with the naked eye. Observing these precautions and using the apparatus mentioned above, separation of copper on the plate took place at once.

That the replacement is not due to the hydrogen developed by the decomposition of the ammonium is shown by the fact that metals like cadmium, and especially zinc, which are not reduced by hydrogen, can be precipitated in this way from solutions of their salts.

The author has thus removed the last experimental evidence against the metallic nature of ammonium.

J. C. W. F.

The Density and Molecular Weight of Ozone.

Since Soret's[1] celebrated work on the density and molecular weight of ozone, carried out more than thirty years ago, no work has been done on this subject until Ladenburg[1] took it up in 1898. Soret worked with a mixture of ozone and oxygen containing only 5 per cent of ozone, and hence Ladenburg deemed it important to redetermine these values, using purer ozone.

---

[1] Ann. Chem. (Liebig), 138, 145; and Suppl., V, 148.

The ozone which he used was generated in a Siemens' ozonizer, whereby a mixture of ozone and oxygen was obtained containing 8 to 9 per cent of the former, which could be easily liquefied in liquid air. The author liquefied such a mixture by means of liquid air, and then allowed the mixture to boil until most of the oxygen had boiled off. A new mixture of liquid ozone and oxygen was added to the residue, and again the oxygen was allowed to boil off. By repeating this operation several times he succeeded in obtaining 2 to 3 cc. of a blackish-blue, non-transparent liquid. He determined the density of the gas obtained when this liquid was vaporized and also the percentage of ozone in it. The density was determined by measuring the time of escape of the gas from a Schilling's apparatus and comparing it with the time of escape of pure oxygen from the same apparatus. The apparatus had been previously tested with pure oxygen and nitrogen, and was found to give very satisfactory results.

Ladenburg thus found that the gas under investigation required four hundred and thirty seconds to escape, while pure oxygen required three hundred and sixty-seven and four-tenths seconds. Hence, the density of the gas was 1.3698, that of oxygen being 1. The percentage of ozone in the gas was determined by titrating, the iodine liberated from a solution of potassium iodide by a known volume of the gas. It was thus found that the gas contained 86.16 per cent by weight of ozone. From these data the density of pure ozone was calculated to be 1.456, that of oxygen being 1, while theoretically it should be 1.5.

Soon after the publication of these results Ladenburg[2] published a note in which he made a correction. In the calculations by which the above results were obtained, he really assumed the molecular weight of ozone to be 48, while this is what he was trying to prove. So he deduced two algebraic equations, which, when solved, gave him 84.4 per cent by weight as the percentage of ozone in his mixture of ozone and oxygen, and 1.469 as the density of pure ozone.

Shortly after this Staedel[3] and Gröger[4] published, at about the same time, criticisms of Ladenburg's work, in which their chief objection was that it is impossible to calculate the density of pure ozone when the density of a mixture of oxygen and ozone and the amount of iodine liberated from potassium iodide only are known. Staedel claimed that Ladenburg assumed ozone to be O_3 and that in one of his equations he assumed the action of ozone on potassium iodide to consist in one atom of the oxygen in ozone liberating two atoms of iodine from the potassium iodide, an assumption which he had no right to make, since he was trying to determine whether ozone is O_3. Gröger expressed the belief that it would be possible to determine the density of ozone only when some absorbent was used which would absorb the ozone entirely without leaving behind a volume of oxygen equal to the volume of ozone started with.

---

[1] Ber. d. chem. Ges., **31**, 2508.
[2] *Ibid.*, **31**, 2830.
[3] *Ibid.*, **31**, 3143.
[4] *Ibid.*, **31**, 3174.

In answering these two criticisms Ladenburg[1] agreed with Staedel and Gröger that the molecular weight of ozone cannot be determined from the density of a mixture of ozone and oxygen and the amount of iodine liberated by such a mixture, but he did not agree that this fact detracted from the value of his results.

He again called attention to the fact that the ozone prepared by him was nearly pure. After the oxygen had boiled off at —186° from the liquid mixture of ozone and oxygen, the thermometer rose 60° without any gas being evolved. The determination of the density of his ozone, which contained a little oxygen, gave the value 1.3698, which corresponds to a molecular weight of 40.8. This showed conclusively, Ladenburg thought, that the molecule of ozone is O_3. If, for instance, it were O_4, there would be an error in his results of over 50 per cent, and the conclusion would follow that his ozone contained 60 per cent of oxygen, for which there was not the slightest evidence.

The determination of iodine liberated from potassium iodide was made merely to ascertain the percentage of ozone in his mixture, which was found to be 84.4 per cent. This value was then used in correcting the density found to that of pure ozone and 1.469 was the result obtained, which corresponds to a molecular weight of 47.

Quite recently Brunck,[2] in an article on the quantitative determination of ozone, referred again to the apparently inadequate proof of Ladenburg that ozone has the molecular weight 48. This reference called forth another reply from Ladenburg,[3] in which he used substantially the same argument which he used against Staedel and Gröger, and further he criticizes some of the results of Brunck regarding the liberation of iodine from potassium iodide in acid solution. Brunck[4] answered these criticisms in a later paper. C. E. C.

---

[1] Ber. d. chem. Ges., **32**, 221.
[2] *Iibd.*, **33**, 1832.
[3] *Ibid.*, **33**, 2282.
[4] *Ibid.*, **33**, 2999.

The Lavoisier Statue in Paris.

On the 27th of July, 1900, a bronze statue of Lavoisier, erected on the Place de la Madeleine, where the residence formerly occupied by him stands, was unveiled in Paris. The statue was designed by Barrias and was purchased with contributions from scientists in all parts of the world. As Moissan said, in presenting the statue to the city: "The master sculptor Barrias has recalled him to us in all the lustre of his power and intelligence. With raised head and extended chest he appers to be answering his detractors and defending his famous theory of combustion." On the pedestal are two high reliefs, one representing him in his laboratory, dictating to his wife the results of his experiments, the other picturing him in the Academy of Sciences explaining to his students his work and his theories. The principal address was made by Berthelot, whose remarks regarding the work of Lavoisier should receive more general notice. On the basis of the great discoveries which have done so much to enrich the world, to improve the industries, and to advance the intellectual and material condition of its inhabitants he regards Lavoisier as worthy of being classed with Galileo, Newton, and Leibnitz.

He says: "Lavoisier has merited the esteem of men, from the philosophical point of view, because he has established the fundamental laws which govern chemical transformations of matter; from the practical point of view, because these laws have become the foundation stone of the innumerable industries based on these transformations. Lavoisier is one of the great benefactors of humanity." He refers to the discovery of the fundamental fact, upon which all the others are based as "that of the chemical constitution of matter and the distinction between ponderable bodies and imponderable ones, as heat, light, and electricity, to whose influence the ponderable ones are exposed. The discovery of this distinction overthrew the old conception of the four elements, corresponding to the four physical states of matter, earth, fire, water, and air, elements which combined in different proportions and according to different laws, to produce all substances known, and to transform one into another." * * "An error not less important than that of transmutation was that of the variability in the weight of bodies exposed to the action of heat, a variation apparently verified by common experience and observation." * * "It is often said that the use of the balance dates only from the last century; but this is an error, as it had been used for centuries and even appeared on the monuments of ancient Egypt." Lavoisier used it to confirm his interpretations of the chemical nature of the act of combustion. "Two causes had tended to delay the true explanation of the facts; the slight knowledge concerning the weights of different gases and the methods of distinguishing one from another, and ignorance regarding the composition of air and water, until then supposed to be undecomposable elements." Lavoisier alone, it is true, did not furnish the evidence necessary to establish the composition of air and water; but profiting by the work of his predecessors and contemporaries he realized the conditions underlying the actions, and was enabled to demonstrate the laws and give the true interpretation. The two great questions, therefore, which Lavoisier settled were, first, what had never before been proved, the distinction between ponderable and imponderable bodies, and, second, the nature of combustion, showing the quantitative relationship between the weights of a gas and a body heated in the gas, and the weight of the final product. These observations led to further experiments and to important deductions regarding the composition of acids and metallic oxides, the composition of air and water, that of organic matter, and the rôle which heat plays in chemical action and in the animal body and the nature of respiration. The observations of Priestley and Black, regarding the necessity of oxygen for respiration and the formation of fixed air, had no apparent connection until Lavoisier applied his combustion theory to the phenomena of respiration and showed the complete analogy between combustion and respiration and the importance of the heat of combustion to the animal body. After referring to other discoveries which were the natural consequences of Lavoisier's work, Berthelot says: "I do not claim that Lavoisier was the personal and direct author of all the discoveries which I have enumerated; but it is certain that he was the one who established the solid foundation upon which the edifice of modern chemistry has been built and without which the discoveries would not have been made." In closing he quotes some remarks of Lavoisier's: "It is not absolutely necessary, in order to merit the esteem of his fellow men and to fulfil his duty to his country, that one should take part in the administration and regeneration of empires. The scientific worker is able, in the quiet of his laboratory, to perform patriotic deeds; he aspires by his work to diminish the suffering of the human race and increase its possessions and happiness and thus to deserve the glorious title of benefactor of the human race."

J. E. G.

AUSGEWÄHLTE METHODEN DER ANALYTISCHEN CHEMIE. Von PROF. A. CLASSEN. Erster Band. Braunschweig: Friedrich Vieweg u. Sohn. 1901. xx + 940 pp.

The general plan of this book is much the same as that of Sir William Crookes' "Select Methods in Chemical Analysis," from which too a considerable part of the matter has been taken. The work is intended mainly for technical chemists and advanced students, so that it assumes a general knowledge on the part of the reader of the commonly employed analytical processes. Special attention is given to the rarer elements, some of which, as for example thorium, have acquired industrial importance of late years. Electrolytic methods for the determination and separation of the metals to which such methods are applicable receive also prominent notice, as might be expected from the long-continued investigations of the author in this direction.

The scope of the book is confined to inorganic chemistry, but, as the title-page gives notice that this is only the first volume, it may be supposed, without any special promise, that hereafter the methods applicable to organic substances will be considered. Some excellent processes are omitted, as for instance the separation by means of amyl alcohol of lithium chloride from the chlorides of sodium and potassium. On the other hand, some of the analytical methods for the examination of industrial products are quite interesting—such as those for the examination of the different kinds of glass, and some of the features of iron and steel analysis as practiced in Germany, which differ from those in general use in America.

The printing and the illustrations are very clear and good.

J. W. M.

THE CHEMICAL ANALYSIS OF IRON. A complete account of all the best known methods for the analysis of iron, steel, pig-iron, iron ore, limestone, slag, clay, sand, coal, coke, and furnace-producer gases. By ANDREW ALEXANDER BLAIR. Fourth edition. Philadelphia and London: J. B. Lippincott Co. 1901.

The fourth edition of Blair's "Chemical Analysis of Iron" appeared in its usual attractive form. The author has wisely decided in this edition to avoid the use of symbols and formulæ in the text, and to adopt a uniformly consistent modern nomenclature. This has necessitated a complete rewriting of the book, which has gained thereby also in minor changes that have been made in arrangement and statement.

This edition preserves the general character of the former ones. No attempt has been made to bring before the busy "iron" chemist the immense number of new processes which appear from year to year in this field of chemical research. To some this will be a matter of regret, while to others the author's restraint will be commended. For, as has been said in notices of previous editions of this work, the book is mainly characterized by being a record of the personal experience and original work of a chemist of strong individuality.

New and valuable matter has indeed been added, notably the method for the determination of phosphorus prepared by the subcommittee of the International Steel Standard Committee of the United States; and the methods for the analysis of coal and coke from the Report of the Committee on Coal Analysis to the American Chemical Society.

A criticism may perhaps be fairly made (although it may possibly seem trivial) on the retention in many places of the subheading "Rapid Methods." The classification of chemical processes on the basis of the time required for their performance is a relic of the day when iron chemists were compelled to hurry their work to satisfy the unreasonable demands of furnace men, and a rapid process was then often synonymous with a hastened process not pretending to the highest accuracy. Now-a-days, however, many of the rapid processes surpass in accuracy the slower ones which they have replaced. In the whole history of analytical chemistry there is nothing more interesting and instructive than the development of the process for the determination of phosphorus whereby results can be obtained in less than an hour which formerly took days, results, too, which in uniformity and accuracy leave nothing to be desired.

This work of Mr. Blair has stood the test of time and remains the first authority in the field of chemical analysis of iron, a model in its clearness of statement and completeness of information.

T. M. DROWN.

Vol. XXV. June, 1901. No. 6.

AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

ON DEHYDROMUCIC ACID.

By Henry B. Hill.

Although dehydromucic acid was first described twenty-five years ago, and already has been made the subject of a number of investigations, a more extended study of it promised to yield interesting results. The chief obstacle to such a study lay in the difficulty of preparing larger quantities of the acid. It was first obtained by Fittig and Heinzelmann,[1] in 1876, by the action of fuming hydrobromic acid under pressure upon mucic acid. The method subsequently given by Heinzelmann,[2] in 1878, was to heat mucic acid for two days in a sealed tube, at 100°, with hydrobromic acid saturated at 0°. The dehydromucic acid which was formed was then separated from the unaltered mucic acid by means of its more readily soluble barium salt. In the following year Seelig[3] found that concentrated hydrochloric acid could be substituted for the hydrobromic acid, and in 1882 Klinkhardt[4] felt justified in recommending a mixture of the two acids as most advantageous. In 1888 Sohst and Tollens[5] found that acid potassic saccharate gave 27.5 per cent of its weight of pure dehydromucic acid when heated for three hours at 150° in a sealed tube with concentrated hydrochloric acid; they also found that a high melting acid was slowly formed by the action of boiling concentrated hydrochloric acid under ordinary pressure. A little later Schrötter[1] showed that dehydromucic acid was formed under these conditions, but that the reaction ran so slowly that after nine days' heating with 30 per cent hydrochloric acid under return condenser a yield of only 16 or 18 per cent of the weight of the potassic saccharate taken could be obtained. Although the method of Schrötter made it possible to prepare larger quantities of the acid in one operation, the long boiling and the comparatively small yield left much to be desired.

---

[1] Ber. d. chem. Ges., **9**, 1198.

[2] Ann. Chem. (Liebig), **193**, 184.

[3] Ber. d. chem. Ges., **12**, 1083.

[4] J. prakt. Chem., [2], **25**, 41.

[5] Ann. Chem. (Liebig), **245**, 19.

In attempting to find a more convenient method of preparation many experiments, which need not be described in detail, were made upon mucic acid and its esters with a variety of dehydrating agents. Although small quantities of dehydromucic acid were in most cases formed, no profitable method for its preparation was found. Our attention was then attracted by the statement of Schmidt and Cobenzl[2] that potassic dehydromucate was formed by the dehydration of neutral potassic mucate at high temperature in a stream of hydrogen. They seem, however, to have made no attempt to identify the salt which they analyzed, or to prepare from it dehydromucic acid. Dr. I. K. Phelps was unable to prepare a neutral potassic mucate containing 2 molecules of water of crystallization, which Schmidt and Cobenzl assert that they used in their experiment, and found that the ordinary anhydrous salt lost in weight very slowly at 200°, while deep-seated decomposition had evidently set in at this temperature. Moreover, it was found that potassic dehydromucate possessed properties entirely different from those which were ascribed by Schmidt and Cobenzl to the salt in question.

We therefore returned to the action of haloid acids and found that boiling concentrated hydrobromic acid at ordinary pressures effected a tolerably rapid conversion of mucic into

[1] Sitzungsber. kk. Acad. Wien, 97, 2b, 407.

[2] Ber. d. chem. Ges., 17, 599.

dehydromucic acid. With saccharic acid, which in the form of its acid potassium salt is even more readily accessible, the reaction ran more rapidly, and after boiling for sixteen hours under return condenser a nearly colorless dehydromucic acid could readily be obtained, which amounted to 25 or 30 per cent of the weight of the saccharate taken. Subsequent experiments showed that this yield could materially be increased by taking a somewhat stronger hydrobromic acid in quantity sufficient to leave a distillable acid after the formation of the potassic bromide.

Dr. I. K. Phelps and Mr. W. J. Hale then studied dehydromucic acid, and prepared certain of its derivatives. Klinkhardt[1] had already established the extreme indifference of the acid toward anhydrous bromine ; further experiments in this direction showed that dehydromucyl chloride was as refractory as the acid itself. No evidence of substitution was obtained on heating the chloride with bromine under the most varied conditions. With aqueous bromine a reaction was noticed analogous to that observed by Hill and Sanger[2] with δ-brompyromucic acid, and afterwards studied by Hill and Hartshorn.[3] The decomposition was most complete in alkaline solution, and yielded then dibromfurfuran tetrabromide and carbonic dioxide. By the action of bromine upon the potassium salt of the acid ethyl ester δ-pyromucic acid was apparently formed. By the action of aluminic chloride upon a solution of the acid chloride in benzol the corresponding diphenyl ketone was readily made. No satisfactory products could be obtained by the reduction of this ketone ; it yielded, on oxidation, as might have been expected, derivatives of benzoic and maleic acids.

More interest attached to the acids formed by the reduction of dehydromucic acid, and their study was undertaken by Mr. A. S. Wheeler.

In 1876 Fittig and Heinzelmann[4] had found that dehydromucic acid was converted into a more readily soluble acid, which melted at about 140°, by the action of sodium amalgam, and three years later Seelig[1] showed, in Fittig's laboratory, that two isomeric acids with the formula $C_6H_6O_5$ could be isolated from the product of this reduction, and that they could be separated through the difference in solubility of their barium salts; Seelig distinguished these two products, which melted at 146° and the second at 173°, as the "hard" and "soft" acids, while Beilstein designated them as the α- and β-acids, respectively. Seelig's description of his results is not always readily intelligible, but his experimental work was evidently done with care and we have been able to confirm substantially all his results. In 1888 Schrötter[2] again studied the reduction of dehydromucic acid and came to the conclusion that the α-acid was the only product of the reaction. While Schrötter is doubtless correct in asserting that the α-acid is the only direct product of the reduction, we have not found it possible to avoid the partial isomerization of this acid, and our product has therefore always contained more or less of the higher melting β-isomer. The quantity of this higher melting acid is very small, if the reduction is carried on at 0°, and the sodic hydrate which is formed is neutralized by a rapid stream of carbonic dioxide; on the other hand it becomes the main product, if the reaction is carried on at ordinary temperature and the sodic hydrate is allowed to accumulate. The isomerization of the pure α-acid is also rapidly effected by warming its alkaline solution. If a strongly alkaline solution of the β-acid is boiled for a long time, a new isomeric acid is formed in quantity.

---

[1] J. prakt. Chem., [2], **25**, 50.

[2] Proc. Am. Acad., **21**, 145 ; Ann. Chem. (Liebig), **232**, 55.

[3] Ber. d. chem. Ges., **18**, 448.

[4] *Ibid.*, **9**, 1199.

This γ-acid shows no sharp melting-point, but decomposes at 190°–200°, according to the rate at which it is heated. While the α- and β-acids cannot be further reduced by sodium amalgam, the γ-acid readily takes two additional atoms of hydrogen and forms the tetrahydrofurfuran dicarboxylic acid, which has recently been described by Lean.[3]

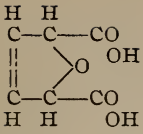
Two structurally isomeric acids can evidently be formed by the addition of two atoms of hydrogen to dehydromucic acid:

---

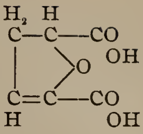
[1] Ber. d. chem. Ges., **12**, 1085.

[2] Sitzungsber. kk. Akad. Wien, **97**, *2b*, 409

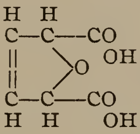
[3] J. Chem. Soc., **77**, 103.



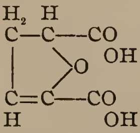
and



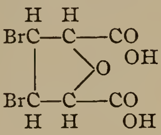
The first of these contains two asymmetric carbon atoms and should give an inactive (cis) form and two optically active (cis-trans) forms. The second formula, with its single asymmetric carbon, gives the possibility of two stereometrically different active modifications and their racemic combination. Our investigation has shown that the α-dihydrofurfuran-αα′-dicarboxylic acid is the cis form of the first structure, the β-acid is the inactive combination of the two active cis-trans forms, while the γ-acid has the second structure formula and is made up of the two possible active bodies. The position of the double bond in the three dihydrofurfuran dicarboxylic acids is sufficiently indicated by the methods of their formation. The α-acid as the first product of the reduction of dehydromucic acid must have the formula



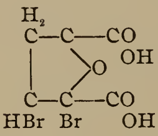
The β-acid probably has the same structure since it is unstable in alkaline solution, while the γ-acid, which is the final product formed by the action of alkalies, undoubtedly has the form



These conclusions are warranted by the facts established by v. Baeyer and his pupils in their study of the analogous reduction of the aromatic acids, and they are confirmed by the behavior of the acids in question. By the prolonged action of sodium amalgam the γ-acid is converted into the corresponding tetrahydrofurfuran dicarboxylic acid, while the α- and β-acids cannot be further reduced; in the case of analogous acids it is established that hydrogen is added to doubly tied carbon atoms under these conditions only when the double bond is adjacent to a carboxyl. Oxidizing agents gave no decisive indication of differences in structure; the chief products in each case were dehydromucic and oxalic acids, although it was noticeable that the α-acid gave the largest yield of dehydromucic acid and the γ-acid gave the smallest. The acids in question readily add bromine, forming products to which the formulæ

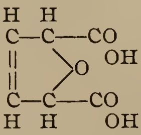


and

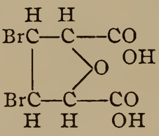


must be assigned.

The α- and β-dibromides are decomposed in alkaline solution in the cold with the elimination of carbonic dioxide and the almost quantitative formation of pyromucic acid; the γ-dibromide also loses carbonic dioxide in alkaline solution, but no pyromucic acid is formed. This reaction leaves no doubt that the α- and β-acids and their dibromides have the identical structures:



and



Since the α- and β-acids were both optically inactive it followed that one of them should be separable into two antipodal active modifications. This conclusion was reached only toward the close of our investigation and we have been able to make but few preliminary experiments in this direction. We have found that the β-acid gives two cinchonine salts of widely different solubility, and that the acids prepared from these salts are optically active with opposite rotations to approximately the same amount. We have not yet prepared the two forms in a pure condition, and must reserve for the future a careful study of the active forms. Our preliminary experiments have also shown us that the γ-acid can be separated into two optically active components.

CXXI.—ON DEHYDROMUCIC ACID AND CERTAIN OF ITS DERIVATIVES.

BY ISAAC K. PHELPS AND WILLIAM J. HALE.

In the course of an extended series of experiments upon the dehydration of mucic acid and its esters it was found that dehydromucic acid was formed on boiling mucic acid with concentrated hydrobromic acid, under a return condenser, and that the formation was sufficiently rapid to serve as a convenient method of preparation. Subsequent experiments showed that the reaction ran much more quickly and completely with saccharic acid, and that the substitution of hydrobromic acid for the 30 per cent hydrochloric acid recommended by Schrötter for this purpose reduced the time necessary to complete the reaction from nine days to sixteen hours, while the yield of dehydromucic acid was very nearly doubled. In the preparation of acid potassic saccharate we have followed the method recommended by Sohst and Tollens.[1] Since the purification of large quantities of the salt by recrystallization is somewhat tedious on account of its slow deposition from solution, we have found it advantageous in the preparation of dehydromucic acid on a large scale to use the crude salt well washed with cold water and freed from the dark-brown mother-liquor by pressure. The saving in time and labor were apparently more than sufficient to compensate us for the diminished yield. At first a distilled hydrobromic acid (sp. gr. 1.49) was used, but later it was found that a stronger acid (sp. gr. 1.56) gave a larger yield; a crude acid made by the alternate addition of bromine and red phosphorus to water could be also used, but the weight of product obtained was then slightly diminished.

---

[1] Ann. Chem. (Liebig), **245**, 3.

The acid potassic saccharate is dissolved in from four to five times its weight of hydrobromic acid, and the solution heated to boiling under a return condenser. Oily drops soon appear in the cooler, carbonic dioxide is given off, and before long the separation of a dark-colored insoluble product begins. The length of time required to complete the reaction varies with the strength of the hydrobromic acid employed; if concentrated acid is used in quantity sufficient to leave an acid saturated at the boiling temperature after the liberation of the saccharic acid from its salt, the decomposition is found already completed at the end of sixteen hours; when distillable hydrobromic acid is used at the outset, the reaction is so nearly finished in this time that longer boiling gives but an insignificant additional product. The dehydromucic acid formed apparently separates completely from the concentrated hydrobromic acid on cooling. Direct experiment showed that distillable acid dissolved at ordinary temperatures about 0.01 per cent of its weight of pure dehydromucic acid, or 15 milligrams to 100 cc. From the black product of the reaction the acid may be extracted by the cautious addition of sodic carbonate, but as a slight excess of the carbonate dissolves also a large amount of coloring-matter, it is much better to make use of the calcium salt. Calcic dehydromucate is much more readily soluble than the barium salt, and on boiling the crude product with water and calcic carbonate, or even with calcic hydrate in excess, little coloring-matter is extracted. The light straw-yellow solution which is obtained yields, on acidification, a slightly colored acid which is sufficiently pure for all ordinary purposes. It may easily be purified by decolorizing with bone-black the solution of its calcium salt.

A number of experiments were made to determine the percentage of dehydromucic acid formed from acid potassic saccharate under different conditions. In each case the crude product was ground up with an excess of calcic carbonate, the mixture boiled with a large amount of water, and the insoluble residue thoroughly extracted with boiling water. The acid was then precipitated from the concentrated solution by the addition of hydrochloric acid and filtered off after standing over night. No correction was made for the solubility of the dehydromucic acid in water; the volume of the mother-liquor and wash-water did not differ widely in the different cases, and it was not easy to determine how far the solubility was modified by the presence of calcic chloride and hydrochloric acid.

The purity of the acid potassic saccharate which was used is shown by the following analyses of two different preparations.

I. 0.5149 gram salt gave 0.1807 gram K_2SO_4.
II. 0.5558 gram salt gave 0.1942 gram K_2SO_4.

	Calculated for $C_6H_9O_8K$.	Found. I.	II.
K	15.77	15.75	15.69

The results of five successive experiments with this pure saccharate are given below. In each case 40 grams of the salt were taken, and the action of the boiling hydrobromic acid continued for sixteen hours. In I. and II. an acid of about 50 per cent was used, which was obtained by the action of red phosphorus upon bromine and water without distillation. In III. a distilled acid of about the same strength was employed. In IV. the same acid was used as in III., but the solution was concentrated by distillation until the boiling-point reached 125° and the original volume of the solution then restored by the addition of fresh distillable acid before boiling with return cooler. In each of these four cases 180 grams of hydrobromic acid were used. In the last case (V.) 195 grams of an acid of sp. gr. 1.565 were taken; on heating, a very small amount of hydrobromic acid escaped through the cooler.

	Weight dehydromucic acid.	Per cent yield.
I.	11.35	28.4
II.	11.50	28.8
III.	11.63	29.1
IV.	13.28	33.2
V.	13.85	34.6

It seemed of interest to make a careful determination of the percentage of dehydromucic acid which could be formed from mucic acid under similar conditions. Accordingly, 30 grams of mucic acid were boiled with 130 grams of distillable hydrobromic acid under return condenser for sixteen hours. The insoluble product was then treated with calcic hydrate and water, and the dehydromucic acid precipitated from the filtered solution. The acid thus thrown down weighed but 6.05 grams, or 20.2 per cent of the mucic acid taken, and in the insoluble lime salt could be found unaltered mucic acid in abundance. It was not possible to determine with precision the amount of mucic acid which had escaped decomposition, but 11.30 grams of ammonic mucate, corresponding to 9.73 grams of mucic acid, were recovered. As a maximum, therefore, but 67.6 per cent of the mucic acid had been decomposed under conditions which apparently bring about the complete decomposition of saccharic acid, while the dehydromucic acid formed amounted to at least 29.9 per cent of the mucic acid which actually entered into reaction. As the mucic acid dissolves quite freely in the boiling hydrobromic acid this slow decomposition can hardly be due to the difference in solubility, but is probably connected with its configuration.

While it would not be profitable to give any account of our many unsuccessful attempts to prepare dehydromucic acid, it seems advisable to describe in some detail certain experiments with potassic mucate, which we were led to undertake by the statement of Schmidt and Cobenzl[1] that potassic dehydromucate could be made by the dehydration of potassic mucate at high temperature in an atmosphere of hydrogen. They analyzed the air-dried mucate which they used and found it to contain a percentage of potassium corresponding to the formula $K_2C_6H_8O_8.2H_2O$, but they make no mention of the previous work of Trommsdorff[2] or Hagen,[3] who found a much higher percentage of potassium in the salt, and they give no description of their method of preparation.

We prepared potassic mucate by the addition of potassic carbonate in slight excess to mucic acid suspended in boiling water. The salt deposited as the solution cooled (I.) or recrystallized from hot water (II.), when air-dried, proved to contain an insignificant amount of water, and essentially the percentage of potassium required by the anhydrous salt. The slight deficit in potassium and the small percentage of water suggested the possible presence of a small amount of the acid salt, which crystallizes with 1 molecule of water. A new preparation was therefore made in precisely the same way except that potassic hydrate was added in considerable excess instead of the carbonate. The salt thus obtained, when well washed with cold water and dried by exposure to the air (III.), gave substantially the same result. The salt obtained by spontaneous evaporation at ordinary temperatures (IV.), or by the precipitation of a cold aqueous solution by the addition of alcohol (V.), also proved to be anhydrous. Finally, a cold saturated solution was partially frozen and the salt which separated with the ice was collected and dried at as low a temperature as we could conveniently command (10° to 12°), but the composition of the salt (VI.) was the same.

---

[1] Ber. d. chem. Ges., **17**, 599.

[2] Gmelin's Handbuch, **5**, 878.

[3] Abhandlung, etc., Berlin, 1849, 5; Gmelin: *Ibid.*

I. 0.3788 gram salt gave 0.2278 gram K_2SO_4; 1.8155 grams of the same salt lost, at 145°, 0.0025 gram H_2O.

II. 0.5000 gram salt gave 0.3015 gram K_2SO_4.

III. 0.3854 gram salt gave 0.2331 gram K_2SO_4.

IV. 0.3846 gram salt gave 0.2327 gram K_2SO_4; 1.4744 grams of the same salt lost, at 145°, 0.0021 gram H_2O.

V. 1.2629 grams salt lost, at 145°, 0.0037 gram H_2O.

VI. 0.3889 gram salt lost, at 145°, 0.0009 gram H_2O; and gave 0.2336 gram K_2SO_4.

	Calculated for		Found.					
	$K_2C_6H_8O_8$.	$K_2C_6H_8O_8.2H_2O$.	I.	II.	III.	IV.	V.	VI.
K	27.34	24.29	27.00	27.07	27.15	27.16	....	26.98
H_2O	....	11.18	0.14	....	....	0.14	0.29	0.23

Although we had not succeeded in preparing a neutral potassic mucate which had the composition assigned to it by Schmidt and Cobenzl, there seemed to be no doubt that the ordinary anhydrous salt could be used equally well for the complete dehydration which they describe, since the hydrous salt must lose its water of crystallization long before any more essential alteration could take place. We therefore heated this salt, contained in a small flask immersed in an oil-bath, in a current of dry hydrogen free from carbonic dioxide; the water and carbonic dioxide formed were then collected in weighed absorption tubes. While Schmidt and Cobenzl found that dehydration was complete at 200°, and that the salt then remained practically unaltered at 240°, we found that the loss of weight below 200° was insignificant, and even at 205° to 210° that water was given off but slowly.

4.5352 grams air-dried salt, when heated for twenty-three hours at 150° to 210°, gave 0.0248 gram CO_2 and 0.1039 gram H_2O.

	Calculated for $K_2C_6H_8O_8$.	Found.
$3H_2O$	18.87	2.29
CO_2	....	0.55

As the dehydration was proceeding so slowly, and deep-seated decomposition had evidently already set in, the heating was discontinued. It seemed best, however, to examine the residual salt carefully for dehydromucic acid, which might possibly have been formed in small quantity. Schmidt and Cobenzl had extracted their dehydrated salt with hot water to remove unaltered potassic mucate, and had recrystallized from boiling water the sparingly soluble residue. On cooling they obtained beautiful white scales, which contained the percentage of potassium required by potassic dehydromucate; but they seem to have made no attempt at a further identification of the salt. On the other hand, our own experiments, which will soon be described, had shown that potassic dehydromucate crystallized in long needles, which were soluble in less than twice their weight of cold water. We therefore examined separately the portions of the heated salt which were most readily and most sparingly soluble in water. Cold water gave an almost black solution, which deposited a dark-colored, flocculent precipitate on acidification. This precipitate was heated with calcic hydrate and water, the solution filtered and evaporated to a small volume; on acidification no dehydromucic acid was deposited. The salt was then extracted with hot water until the greater part had gone into solution. As the residue still appeared to be potassic mucate, it was acidified with hydrochloric acid and the acid obtained treated with calcic hydrate as before; but in this case also the acidified solution remained perfectly clear. When 0.01 gram of dehydromucic acid was mixed with 1 gram of mucic acid and the mixture was treated in the same way with calcic hydrate, enough dehydromucic acid could easily be recovered to identify it by means of its characteristic reaction with ferric chloride. We must conclude, therefore, that no sensible amount of dehydromucic acid had been formed from potassic mucate after heating for twenty-three hours; for seventeen hours the temperature had been held at 200° to 210°.

Potassic Dehydromucate, $K_2C_6H_2O_5.H_2O$.—As this salt had not previously been described it was prepared by adding potassic carbonate in slight excess to dehydromucic acid suspended in a little water. The concentrated solution gradually solidifies with the separation of slender prisms, but the salt may be obtained more conveniently by the addition of alcohol to the aqueous solution. From hot 75 per cent alcohol it crystallizes in long silky needles, which dissolve in less than twice their weight of cold water.

I. 0.3498 gram of the air-dried salt gave 0.2439 gram K_2SO_4.

II. 2.0986 grams air-dried salt lost at 200° 0.1483 gram H_2O.

	Calculated for $K_2C_6H_2O_5.H_2O$.	Found.	
		I.	II.
K	31.28	31.30	....
H_2O	7.20	....	7.07

Determinations of the solubility of the acid and its barium salt, which we owe to Mr. A. S. Wheeler, may best find place here; we add our own determination of the solubility of the calcium salt.

Dehydromucic Acid.—The saturated solution of the acid was boiled with baric carbonate, and the barium precipitated with sulphuric acid from the filtered solution.

I. 45.95 grams solution, saturated at 18°, gave 0.0693 gram $BaSO_4$.

II. 48.65 grams solution, saturated at 18°, gave 0.0722 gram $BaSO_4$.

According to these determinations the solution saturated at 18° contained the following percentages of the acid:

I.	II.
0.101	0.099

Baric Dehydromucate.—The barium was determined by precipitation.

I. 43.79 grams solution, saturated at 18°, gave 0.3190 gram $BaSO_4$.

II. 42.96 grams solution, saturated at 18°, gave 0.3127 gram $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.91	0.91

Calcic Dehydromucate.—The calcium in the saturated solution was determined by evaporation with sulphuric acid.

I. 9.347 grams solution, saturated at 18°, gave 0.2576 gram $CaSO_4$.

II. 9.573 grams solution, saturated at 18°, gave 0.2647 gram $CaSO_4$.

The aqueous solution saturated at 18° therefore contains the following percentages of the anhydrous salt.

I.	II.
3.93	3.94

This solubility is approximately doubled by heating the solution to boiling.

Monomethyl Dehydromucate, $C_7H_6O_5$.—This body was made by allowing 1 molecule of potassic hydrate to act upon dimethyl dehydromucate[1] dissolved in methyl alcohol. At ordinary temperature the alkaline reaction gradually disappears and the acid ester may then be precipitated from the concentrated solution by the addition of hydrochloric acid. It may easily be purified by recrystallization from hot water.

0.1346 gram substance gave 0.2442 gram CO_2 and 0.0446 gram H_2O.

	Calculated for $C_7H_6O_5$.	Found.
C	49.42	49.50
H	3.56	3.71

---

[1] Zenoni (Gazz. chim. ital., 20, 519) gives the melting-point of the dimethyl ester as 112°. After repeated recrystallization, or sublimation, we have found the melting-point constant at 109° to 110° (corr.).

The monomethyl dehydromucate is readily soluble in alcohol or ether, sparingly soluble in chloroform, and insoluble in benzol or ligroin. It dissolves freely in hot water, and as the solution cools is deposited in lustrous leaflets which melt at 201° to 202° (corr.).

Monoethyl Dehydromucate, $C_8H_8O_5$.—The diethyl ester was allowed to stand in alcoholic solution with 1 molecule of potassic hydrate until the alkaline reaction had disappeared. The alcohol was then expelled by heat with the addition of water, the aqueous solution filtered and acidified. The product thus obtained was recrystallized from hot water.

0.2200 gram substance gave 0.4216 gram CO_2 and 0.0898 gram H_2O.

	Calculated for $C_8H_8O_5$.	Found.
C	52.16	52.28
H	4.38	4.57

The monoethyl dehydromucate is readily soluble in alcohol, more sparingly soluble in ether, sparingly soluble in chloroform or benzol, and insoluble in ligroin. It is readily soluble in hot water and separates, as the solution cools, in clustered needles which melt at 148° to 149° (corr.).

Dehydromucic Acid Amide, $C_6H_5NO_4$.—Ammonic hydrate in concentrated solution readily converts the acid ethyl ester into the corresponding amide, and the reaction is completed at ordinary temperatures in the course of twenty-four hours. The acid amide is insoluble in the ordinary organic solvents, but crystallizes well from hot water in the form of long slender needles, which melt at 280° to 281° (corr.).

0.2246 gram substance gave 17.8 cc. moist nitrogen at 21°.5 and under a pressure of 774 mm.

	Calculated for $C_6H_5NO_4$.	Found.
N	9.06	9.13

Dehydromucic Dianilide, $C_6H_2O_3(NHC_6H_5)_2$.—A slight excess of aniline was added to dehydromucyl chloride dissolved in eight times its weight of ether, and the product, which was at once formed, was crystallized from 50 per cent alcohol after washing well with water; it crystallizes in long, radiating needles, which melt at 227° to 228° (corr.). The body is practically insoluble in ether, ligroin, or boiling water; it is very sparingly soluble in benzol, somewhat more readily soluble in chloroform, but readily soluble in alcohol.

0.1606 gram substance gave 12.8 cc. moist nitrogen at 20°.5 and under a pressure of 770 mm.

	Calculated for $C_{18}H_{14}N_2O_3$.	Found.
N	9.18	9.18

Dehydromucicdiacetic Anhydride, $C_{10}H_8O_7$.—When dehydromucic acid is heated under return condenser with an excess of acetic anhydride[1] it gradually goes into solution, and on cooling colorless leaflets of the mixed anhydride are deposited. The body may be recrystallized from hot acetone or benzol. It is sparingly soluble in ether or ligroin, more readily soluble in boiling benzol, acetone, ethyl acetate, glacial acetic acid, or chloroform. The melting-point of the substance could not be determined since it is rapidly decomposed at about 150° with the formation of acetic anhydride.

0.1634 gram substance gave 0.2988 gram CO_2 and 0.0500 gram H_2O.

	Calculated for $C_{10}H_8O_7$.	Found.
C	49.99	49.87
H	3.36	3.42

The molecular weight of the substance was determined by means of the boiling-point of the solution in benzol with the following results:

Substance.	Solution.	Elevation.	Molecular weight.
0.1312	18.85	0.075	247.8
0.1196	18.75	0.068	250.5
0.1500	18.65	0.087	246.8

Dehydromucic Anhydride, $C_{12}H_4O_8$(?).—By the rapid heating of dehydromucic acid with phosphoric pentachloride Klinkhardt[2] obtained an amorphous, sublimable body, soluble in alcohol, which he thought might possibly be the anhydride of the acid, but he did not examine the substance more carefully. On repeating the experiments of Klinkhardt we have not succeeded in isolating any definite product except the chloride of the acid. On heating this acid chloride with 1 molecule of the acid or of its salts, we obtained no satisfactory results, and Klinkhardt had already found that dehydromucic acid was converted into its chloranhydride when it was heated with acetyl chloride. When the diacetic anhydride which has just been described was heated to 150° most conveniently under diminished pressure, we found that decomposition took place, that acetic anhydride distilled off, and that the pale-yellow residue which remained had the composition required by dehydromucic anhydride. The substance proved to be practically insoluble in all ordinary solvents, and by heat it was decomposed without melting. Under diminished pressure the slow formation of a crystalline sublimate was noticed at high temperature, but purification by sublimation appeared to be impracticable. The substance was therefore extracted successively with boiling acetic anhydride and acetone, and analyzed with no attempt at further purification.

---

[1] Schrötter states (*Loc. cit.*, 410) that acetic anhydride has no action upon dehydromucic acid.

[2] J. prakt. Chem., [2], **25**, 46.

I. 0.1730 gram substance gave 0.3298 gram CO_2 and 0.0292 gram H_2O.

II. 0.1800 gram substance gave 0.3420 gram CO_2 and 0.0276 gram H_2O.

	Calculated for $C_6H_2O_4$.	Found. I.	Found. II.
C	52.17	52.01	51.82
H	1.46	1.89	1.71

The dehydromucic anhydride was very slowly attacked by boiling water, but hot caustic alkalies soon carried it into solution. The physical properties of the body were such that its molecular weight could not be determined directly; it seems probable, however, that it is formed from 2 molecules of the acid.

Action of Halogens.

The behavior of dehydromucic acid towards dry bromine was investigated by Klinkhardt, who found that no addition-product could be formed, and that no substitution took place when the acid was heated with bromine. It seemed advisable to make further experiments in this direction under conditions which are ordinarily more favorable to the formation of substitution-products. The acid chloride melting at 80° was accordingly heated with bromine, in a sealed tube, to 250°, but no hydrobromic acid was formed and no change was apparent. On heating the mixture in direct sunlight, or with the addition of bromides of aluminium or phosphorus under varied conditions, we were equally unsuccessful.

Klinkhardt had already shown that fumaric acid is formed by the action of aqueous bromine, but we were interested to know whether, under favorable conditions, substituted furfurans could not be formed as Hill and Sanger[1] had shown to be the case with δ-brompyromucic acid. Four molecules of bromine were therefore added to an aqueous solution of potassic dehydromucate and the product which separated on standing collected by extraction with ether. The product was partially soluble in hot ligroin, and as the solution cooled dibromfurfurantetrabromide separated, which melted at 111° after several recrystallizations from ligroin. The portion of the product which was insoluble in ligroin was recrystallized from hot water, and recognized from its crystalline form and its behavior in capillary tube as ordinary dibromsuccinic acid. The formation of the dibromsuccinic acid could almost entirely be avoided by the addition of an excess of potassic carbonate to the dilute solution of the dehydromucate and then adding the bromine slowly with constant shaking. From 2 grams of dehydromucic acid 3 grams of dibromfurfurantetrabromide were then obtained. After several recrystallizations from ligroin it melted at 112° and gave, with alcoholic potassic hydrate, the tetrabromfurfuran melting at 65°.

0.1096 gram substance gave 0.2266 gram AgBr.

	Calculated for $C_4H_2Br_6O$.	Found.
Br	87.90	87.98

Iodine also reacts upon potassic dehydromucate with the formation of diiodfurfuran, but the reaction takes place promptly only at temperatures above 100°. Two molecules of iodine were added to an aqueous solution of potassic dehydromucate, together with potassic iodide in sufficient quantity to carry the iodine into solution. After heating for two hours at 120°, the solution was found to be decolorized and an insoluble product had separated. This product was then collected in ether, and the pale yellow residue left by the ether recrystallized from dilute alcohol. The body thus obtained crystallized in colorless plates, which melted at 47° and gave the percentage of iodine required by a diiodfurfuran.

---

[1] Proc. Am. Acad., **21**, 145; Ann. Chem. (Liebig), **232**, 55.

0.1002 gram substance gave 0.1471 gram AgI.

	Calculated for $C_4H_2I_2O$.	Found.
I	79.34	79.32

This αα'-diiodfurfuran is readily soluble in all ordinary organic solvents, but may be crystallized from dilute alcohol. With bromine it yields at once dibromfurfuran tetrabromide with the separation of iodine.

We were further interested to investigate the action of bromine upon an alkaline solution of monoethyl dehydromucate. Although we did not succeed in finding the conditions necessary to give a smooth reaction our results leave no doubt that δ-brompyromucic acid is thus formed. If a solution of monoethyl dehydromucate is made alkaline with potassic carbonate and 1 molecule of bromine is then added, the liquid soon grows turbid with the separation of a colorless oil. This oil, when extracted with ether, was found to possess the characteristic odor of ethyl δ-brompyromucate and solidified at low temperature. On the addition of alcoholic potassic hydrate a crystalline potassium salt was formed. The acid liberated with hydrochloric acid was sparingly soluble in cold water, and crystallized from hot water in shining leafy plates, which melted at 182°. According to Hill and Sanger[1] brompyromucic acid melts at 183° to 184° and its ethyl ester at 17°.

We also attempted to prepare in the same way the corresponding iodine derivative of pyromucic acid, but without success.

αα'-Dibenzoyl Furfuran, $C_{18}H_{12}O_3$.—This ketone may easily be made by acting upon a solution of dehydromucyl chloride in benzol with aluminic chloride. Several different methods of preparation were tried, and the best results were obtained in the following manner: 27 grams of the acid chloride were dissolved in 40 grams of benzol and the solution allowed to drop slowly into a boiling solution of 50 grams of aluminic chloride in an equal weight of benzol. After the reaction was over the product was isolated in the usual way and recrystallized from ligroin or alcohol. The weight of the ketone obtained was at least equal to that of the acid chloride taken, and in the case given above the yield was 37 grams, or 96 per cent of the theoretical amount.

---

[1] *Loc. cit.*

I. 0.2026 gram substance gave 0.5843 gram CO_2 and 0.0881 gram H_2O.

II. 0.2038 gram substance gave 0.5871 gram CO_2 and 0.0880 gram H_2O.

	Calculated for $C_{18}H_{12}O_3$.	Found.	
		I.	II.
C	78.26	78.65	78.57
H	4.38	4.86	4.83

The αα′-dibenzoyl furfuran crystallizes from alcohol or ligroin in lustrous needles, which melt at 107° (corr.) and sublime at higher temperature. It is readily soluble in cold benzol, chloroform, or glacial acetic acid, sparingly soluble in cold ligroin or carbonic disulphide, somewhat less sparingly soluble in cold alcohol; it is also sparingly soluble in ether.

By the action of various reducing agents upon the ketone we were unable to obtain any well-defined products. Even with red phosphorus and hydriodic acid an amorphous, sticky body was obtained which did not invite further study. With dry bromine, substitution slowly takes place, and a bromine derivative of high melting-point is formed which we have not further examined. Aqueous bromine has little effect under ordinary pressures, but at 140°, in a sealed tube, reaction sets in and dibrommaleic and brombenzoic acids are formed. The acids were extracted with sodic carbonate, the solution filtered from the unaltered ketone, and acidified. The acid which separated melted at 140° to 141° and contained the percentage of bromine required by a brombenzoic acid.

0.1530 gram substance gave 0.1436 gram AgBr.

	Calculated for $C_7H_5BrO_2$.	Found.
Br	39.78	39.94

A closer examination of this acid showed that it contained all three isomers. From the sparingly soluble barium salt was obtained an acid which melted at 153° (uncorr.) after one recrystallization from water, and which was therefore *m*-brombenzoic acid. The readily soluble barium salt yielded a sparingly soluble acid which melted at 245° (uncorr.), and a more readily soluble acid which melted at 142° to 143° (uncorr.); these were evidently the para and ortho acids which melt at 251° and 147°, respectively. The acid liquid from which the brombenzoic acids had separated was extracted with ether and the ether evaporated. The crude acid thus obtained was neutralized with baric hydrate, and the barium salt precipitated from aqueous solution by the addition of a small amount of alcohol. The salt, when recrystallized from water, had the characteristic form of baric dibrommaleate, and the acid prepared from it could be converted by sublimation into the flattened needles of the dibrommaleic anhydride melting at 113°.

On boiling the ketone with diluted nitric acid (sp. gr. 1.30) no action was observed, and the oxidation was not well marked until the specific gravity of the nitric acid reached 1.40. After boiling with an acid of this strength for five hours, the excess of the nitric acid was driven off and the residue extracted with sodic carbonate. A large part of the product proved to be insoluble in the alkaline solution, but this neutral body dissolved readily in alcohol, leaving a very small quantity of a white crystalline substance, which melted at 194° to 195° (uncorr.). The alcoholic solution, when mixed with glacial acetic acid, deposited a crystalline body which was readily soluble in cold benzol or chloroform, insoluble in carbonic disulphide, but which could be recrystallized from alcohol. The body then melted at 130° to 131° (uncorr.), and contained a percentage of nitrogen which showed that it was a mononitro derivative of the ketone; it was not further studied.

0.2002 gram substance gave 8.5 cc. moist nitrogen at 27° and under a pressure of 756 mm.

	Calculated for $C_{18}H_{11}NO_5$.	Found.
N	4.37	4.64

The acids formed by the action of the nitric acid upon the ketone were precipitated from the alkaline solution on the addition of hydrochloric acid. An analysis of the silver salt gave a percentage of silver which agreed with that required by an argentic nitrobenzoate.

0.1095 gram salt gave 0.0747 gram AgBr.

	Calculated for $AgC_7H_4NO_4$.	Found.
Ag	39.39	39.18

Fractional crystallization of the barium salt showed that it was a mixture of the three possible isomers. The readily soluble part of the salt yielded an acid melting at 143° to 144° (uncorr.), which was evidently the *o*-nitrobenzoic acid; the most sparingly soluble salt gave the meta acid melting at 139° (uncorr.), while from the intermediate portion an acid was obtained which melted at 220° to 225° (uncorr.), and which was therefore essentially the *p*-nitrobenzoic acid.

αα'-Dibenzoyl Furfuran Diphenylhydrazone, $C_{30}H_{24}N_4O$.—The ketone was dissolved in fourteen times its weight of glacial acetic acid, an excess of phenylhydrazine added, and the solution heated for some time on the water-bath. On cooling, the dihydrazone separated in bright-yellow, finely felted needles which were recrystallized from hot glacial acetic acid.

0.2207 gram substance gave 25.6 cc. moist nitrogen at 25° and under a pressure of 758 mm.

	Calculated for $C_{30}H_{24}N_4O$.	Found.
N	12.31	12.84

The dihydrazone is readily soluble in chloroform or benzene, but sparingly soluble in alcohol, ether, or glacial acetic acid. When quickly heated it melts promptly at 155° to 156° (corr.), but when slowly heated it melts at a much lower temperature.

αα'-Dibenzoyl Furfuran Dioxime, $C_{18}H_{14}N_2O_3$.—Hydroxylamine reacts readily upon the ketone in alcoholic solution when an excess of sodic hydrate is added as recommended by Auwers.[1] We have added to the ketone, suspended in fifteen times its weight of alcohol, 3 molecules of hydroxylamine hydrochlorate and 6 molecules of sodic hydrate, each dissolved in a little water. The reaction soon begins and is apparently completed on long standing at ordinary temperatures, but we have usually heated the mixture for several hours on the water-bath. After the evaporation of the alcohol, with the addition of water, the oxime was precipitated with carbonic dioxide. The weight of the product obtained was somewhat greater than that of the ketone taken and amounted to 93.5 per cent of the calculated weight of dioxime. The behavior of the substance in a capillary tubes led us to think that it was not homogeneous, and on crystallization from alcohol it proved to contain at least two different bodies, one of which crystallized in long, slender needles, the other in small, granular aggregations. The solubility of these two bodies in alcohol did not differ sufficiently to enable us to separate them sharply, but no other solvent was found which would answer the purpose better. The most satisfactory method of separation which we have discovered depends upon the different solubilities of the sodium salts of the two bodies in dilute solutions of sodic hydrate, and the readiness with which one of these salts is hydrolyzed in dilute aqueous solution. The hydrolytic dissociation of the sodium salts of oximes was suggested by V. Meyer[1] for the separation of isomeric forms. While the method we describe leaves much to be desired, it has enabled us to separate two bodies which differ widely in properties, and the intermediate fractions have given every indication that they are made up of mixtures of these two substances alone.

---

[1] Ber. d. chem. Ges., **22**, 604.

The mixed oximes are suspended in a little water and rather more than 2 molecules of sodic hydrate added in concentrated solution. To the gently warmed, clear solution is then added rather less than 4 molecules of sodic hydrate, the concentration being so adjusted that each cubic centimeter of the final solution contains about 150 milligrams of the mixed oximes and 120 milligrams of sodic hydrate. On standing, a crystalline sodium salt separates which is collected after the lapse of twenty-four hours, washed with a little double normal sodic hydrate and drained as completely as possible on the pump. The salt thus obtained dissolves readily in a small amount of warm water, but if the solution is diluted hydrolytic dissociation takes place, slowly at ordinary temperatures; rapidly on heating with the separation of the clustered needles of the α-dioxime. The alkaline solution from which the α-dioxime has thus separated contains both forms of the dioxime, which are then precipitated together by carbonic dioxide and again dissolved in sodic hydrate of the proper concentration. The original alkaline mother-liquor, from which the α-sodium salt has crystallized, contains chiefly the β-dioxime, but we have found no method for its purification beyond the removal of the α-dioxime as completely as possible by the use of a still more concentrated solution of sodic hydrate and the repeated recrystallization from alcohol of the oxime thrown down by carbonic dioxide from this strongly alkaline solution.

---

[1] Ann. Chem. (Liebig), 264, 116.

Both forms of the dioxime are readily soluble in acetone or ethyl acetate, and are precipitated from these solutions on the addition of ligroin. They are both sparingly soluble in alcohol, although the α-dioxime dissolves the more freely, and still more sparingly soluble in ether, chloroform, or benzol. We have not succeeded in preparing any derivatives which could be utilized in their separation or identification. We have also as yet been unable to obtain definite products from Beckmann's molecular rearrangement; the α-dioxime here is apparently converted into the more stable β-modification, and the same conversion may be brought about by heat.

The analysis of the α-dioxime gave the following results:

I. 0.2365 gram substance gave 0.6118 gram CO_2 and 0.1046 gram H_2O.

II. 0.2014 gram substance gave 16.4 cc. moist nitrogen at 15° and under a pressure of 749 mm.

	Calculated for $C_{18}H_{14}N_2O_3$.	Found. I.	II.
C	70.57	70.57	....
H	4.61	4.95	....
N	9.18	....	9.35

The α-dioxime crystallizes from hot alcohol in long, slender needles, which melt at 213°–214° (uncorr.) when quickly heated. The melted substance occasionally solidifies again at higher temperature, or if solidified by cooling it melts at a higher point. The pure substance was therefore quickly melted and immediately cooled. The hot alcoholic solution then deposited with the needles of the α-dioxime the granular aggregations of the β-modification. A partial separation through the sodium salts showed that the latter amounted to at least 40 per cent of the α-dioxime taken, and the body, after one crystallization from alcohol, melted at 241° to 243° (uncorr.).

The β-dioxime, separated as completely as possible from the α-modification by the process just described, was precipitated with carbonic dioxide, extracted with small quantities of boiling alcohol, and finally recrystallized from a larger amount of the same solvent. It is deposited in minute, irregular plates which are usually grouped in granular clusters. When quickly heated it melted at 243° to 245° (uncorr.); but at this temperature decomposition sets in almost immediately, and the melting-point was much lower if the substance was slowly heated.

I. 0.2316 gram substance gave 0.5972 gram CO_2 and 0.1018 gram H_2O.

II. 0.2062 gram substance gave 17.2 cc. N over KOH (1 : 2) at 18°.5 and under a pressure of 750 mm.

	Calculated for $C_{18}H_{14}N_2O_3$.	Found. I.	II.
C	70.57	70.35	....
H	4.61	4.92	....
N	9.18	....	9.51

CXXII.—ON THE REDUCTION OF DEHYDROMUCIC ACID.[1]

By HENRY B. HILL AND ALVIN S. WHEELER.

In repeating the work of Seelig upon the reduction of dehydromucic acid we were able to profit by the results obtained in recent years by v. Baeyer and his pupils in the study of the reduction of the analogous aromatic dibasic acids. In the light of their experience there seemed to be little doubt that Seelig's acid melting at 146° was the direct product of the reduction, and that the isomeric acid melting at 173° was formed from it by the action of the sodic hydrate set free in the reaction. That Schrötter was unable to isolate the second form of the acid was then due in part to his method of reduction, and in part to an insufficient examination of his product. Seelig used a large excess of sodium amalgam, at ordinary temperature, without neutralizing the sodic hydrate which was formed. We reduced the sodium to one-fifth the amount used by him, carried on the reaction at 0°, in a much more concentrated solution, and at the same time passed a rapid stream of carbonic dioxide into the solution. Under these conditions but little of the higher melting isomer was formed. The latter acid becomes the main product, if the reduction is carried on at ordinary temperature without neutralizing the sodic hydrate, and the alkaline solution is then heated to boiling. Reduction is readily effected when the dehydromucic acid is suspended in ten times its weight of water, neutralized with sodic carbonate, and thirty-five times its weight of finely divided 3 per cent sodium amalgam added. The time required to complete the reaction depends upon the subdivision of the amalgam, but is usually about two hours. Since the products of the reduction are readily soluble in water the reaction is very nearly completed as soon as hydrochloric acid fails to precipitate any unaltered dehydromucic acid. We have also reduced dehydromucic acid by the electrolysis of a solution of its sodium salt containing 10 per cent of the acid. This mode of reduction, however, did not appear to us to offer any advantage over the use of sodium amalgam.

---

[1] The work described in the following paper formed a part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, in May, 1900, by Alvin S. Wheeler, candidate for the degree of doctor of philosophy.

The isolation of the acids which are formed was at first a matter of some difficulty. Although they may be extracted from aqueous solution by ether, the process is slow and involves a great deal of labor by the ordinary method with separatory funnel. Evaporation to dryness and extraction of the pulverized residue in a Soxhlet extractor was more advantageous, but still far from convenient. The method finally adopted was the use of a slightly modified form of automatic extractor for liquids described by Göckel.[1] The side tube recommended by Göckel seemed to us a needless complication, and we found a plain straight jacket-tube to answer the purpose admirably. The alkaline solution, poured off from the mercury, was made feebly acid to litmus, concentrated to a convenient volume, strongly acidified with hydrochloric acid, and completely extracted with ether. So efficient was the automatic extractor that 89 per cent of the lower-melting (α)-acid contained in the solution could be extracted in five hours. A partial separation of the two isomeric acids can be effected in the course of the extraction, since the α-acid is more readily taken up, and the product obtained toward the end of the extraction is mainly β-acid. The crude acid left by the evaporation of the ether formed a light-colored, crystalline mass, while Seelig obtained a syrup which slowly crystallized when allowed to stand in a desiccator. It seems to us probable that his product contained, in addition to the two acids which he described, the γ-acid which we mention later, and possibly also the tetrahydrofurfuran-$\alpha\alpha'$-dicarboxylic acid formed from this acid by reduction. The weight of the product which we obtained was very nearly that required by theory.

---

[1] Zeit. angew. Chem., 1897, 683; Chem. Centrbl., 1897, II., 1169.

In the separation of the two isomeric acids which form the main part of the product we used at first the barium salts as recommended by Seelig; a more careful study showed us that the lead salts were far better adapted to the purpose. If the mixed acids are dissolved in thirty times their weight of water and the solution boiled with baric carbonate, a solution is obtained which deposits, on cooling, the pulverulent salt of the α-acid. On spontaneous evaporation six-sided plates separate, which are also a salt of the α-acid, but with 4.5 molecules of water, while the pulverulent salt contains two. When the solution is then concentrated to small volume it becomes pasty with the separation of the salt of the β-acid, necessarily with some admixture of the α-salt. The mother-liquor, by spontaneous evaporation, then leaves a varnish which resembles that given under like conditions by a solution of the barium salt of the γ-acid. While the sparingly soluble salt of the α-acid could easily be purified by recrystallization, the more soluble salt of the β-acid could not readily be isolated in a pure condition. Although the difference in the solubility of the lead salts of the two acids at ordinary temperatures proved to be less than that of the barium salts, the solubility of the salt of the α-acid was largely increased by heat, while that of the salt of the β-acid was little more than doubled. The crude acid was therefore dissolved in about one hundred times its weight of water, boiled with an excess of plumbic carbonate and the hot solution stirred to promote the separation of the salt of the β-acid. The solution quickly filtered then deposited almost the whole of the salt of the α-acid in the form of bulky needles, which may be purified by recrystallization from boiling water. On treating the β-salt with small quantities of boiling water all admixture of the more soluble α-salt is removed. Although we have found it easy to prepare a crude acid which should contain chiefly one isomer or the other, a careful examination has invariably shown both acids present. While the γ-acid was also probably present, especially when the β-acid was the chief product, the quantity was so small that it gave no trouble. In the preparation of the γ-modification we have taken pains to carry the reaction so far that all the β-acid was isomerized.

α-Dihydrofurfuran-αα′-dicarboxylic Acid.

The preparation of the lead salt of this acid has just been described. We have usually suspended the salt in water, set free the acid with hydrogen sulphide, evaporated the aqueous solution to dryness, and recrystallized the residue from ether. If the reduction is carried on at 0° and a rapid stream of carbonic dioxide is passed into the solution, almost the whole product consists of this acid. It dissolves in about twice its weight of cold water and is still more readily soluble in hot water ; from aqueous solution it crystallizes in friable, leafy plates, which are anhydrous. It dissolves readily in alcohol or in ether and frequently crystallizes from the latter solvent in large, rectangular plates ; it is very sparingly soluble in chloroform and insoluble in benzol or ligroin ; from a mixture of ether and ligroin it crystallizes in the form of needles. The pure acid melts at 149° to 150° (corr.).

An analysis gave the following results :

0.2108 gram substance gave 0.3526 gram CO_2 and 0.0715 gram H_2O.

	Calculated for $C_6H_6O_5$.	Found.
C	45.55	45.62
H	3.83	3.79

The barium, calcium, and silver salts of the acid were analyzed by Seelig ; we have repeated his work and also studied the lead salt.

Baric α-Dihydrofurfuran-αα′-dicarboxylate, $BaC_6H_4O_5.2H_2O$. The acid was dissolved in thirty times its weight of water and the solution boiled with an excess of baric carbonate. As the filtered solution cools, the greater part of the salt separates in a finely divided condition. The air-dried salt proved to contain 2 molecules of water.

I. 0.3252 gram air-dried salt gave 0.2294 gram $BaSO_4$.

II. 1.1542 grams air-dried salt lost, at 180°, 0.1318 gram H_2O.

	Calculated for $BaC_6H_4O_5.2H_2O$.	Found.	
		I.	II.
Ba	41.71	41.52	....
H_2O	10.93	....	11.42

If a cold solution of this salt is allowed to evaporate spontaneously, large, six-sided plates are deposited which contain 4.5 molecules of water.

1.0122 grams air-dried salt lost, at 190°, 0.2164 gram H_2O.

	Calculated for $BaC_6H_4O_5.4\frac{1}{2}H_2O$.	Found.
H_2O	21.65	21.38

Both of these salts were obtained and analyzed by Seelig.

A cold saturated solution obtained by cooling a hot solution of the barium salt gave the following results :

I. 42.07 grams solution, saturated at 18°, gave 0.0700 gram $BaSO_4$.

II. 48.97 grams solution, saturated at 18°, gave 0.0799 gram $BaSO_4$.

The aqueous solution saturated at 18° therefore contained the following percentages of the anhydrous salt :

I.	II.
0.21	0.20

Calcic α-Dihydrofurfuran-αα′-dicarboxylate, $CaC_6H_4O_5.1\frac{1}{2}H_2O$.—This salt was very readily soluble in water and it was necessary to evaporate the solution to small volume in order to ensure its separation. As the salt proved to be deliquescent, a fact not mentioned by Seelig, it was dried by pressure between folds of filter-paper and analyzed at once. Our analysis showed that it contained but 1.5 molecules of water, while Seelig had found 2.5.

1.0897 grams salt lost, at 180°, 0.1270 gram H_2O.

	Calculated for.	Found.
H_2O	12.12	11.65

0.2062 gram salt, dried at 180°, gave 0.1436 gram $CaSO_4$.

	Calculated for.	Found.
Ca	20.40	20.46

Argentic α-Dihydrofurfuran-αα′-dicarboxylate, $Ag_2C_6H_4O_5.\frac{1}{2}H_2O$.— Our analyses of the air-dried silver salt confirmed the conclusion of Seelig that it contained 0.5 molecule of water which could not be expelled by heat without decomposition. At 125° it lost but 0.38 per cent of its weight, while the calculated loss for 0.5 molecule of water is 2.36 per cent; even at this temperature decomposition soon set in.

0.2169 gram air-dried salt gave 0.1632 gram AgCl.

	Calculated for $AgC_6H_4O_5.\frac{1}{2}H_2O$.	Found.
Ag	56.66	56.62

Plumbic α-Dihydrofurfuran-αα′-dicarboxylate, $PbC_6H_4O_5.2H_2O$.—This salt was made by neutralizing with plumbic carbonate a boiling solution of the acid in one hundred times its weight of water. As the filtered solution cools the salt separates in bulky, opaque needles which, on long standing, are converted into compact, transparent plates. Occasionally these plates were formed at first on slow cooling of the solution. Analyses showed that the two forms of the salt had the same composition.

I. 1.4919 grams air-dried needles lost, at 180°, 0.1371 gram H_2O.

II. 1.1808 grams air-dried plates lost, at 165°, 0.1090 gram H_2O.

	Calculated for $PbC_6H_4O_5.2H_2O$.	Found. I.	Found. II.
H_2O	9.01	9.19	9.23

0.2988 gram anhydrous salt gave 0.2494 gram $PbSO_4$.

	Calculated for $PbC_6H_4O_5$.	Found.
Pb	57.01	57.01

The solubility of the salt in hot water was determined according to the method described by Pawlewski,[1] in addition to its solubility at ordinary temperature. In each case the lead was precipitated as sulphide and weighed as sulphate.

I. 49.69 grams solution, saturated at 20°, gave 0.0191 gram $PbSO_4$.

II. 48.52 grams solution, saturated at 20°, gave 0.0187 gram $PbSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt.

I.	II.
0.046	0.046

I. 7.470 grams solution, saturated at 99°.5, gave 0.0634 gram $PbSO_4$.

II. 10.077 grams solution, saturated at 99°.5, gave 0.0870 gram $PbSO_4$.

The aqueous solution saturated at 99°.5 therefore contained the following percentages of the anhydrous salt:

I.	II.
1.02	1.03

When the α-*Dihydrofurfuran*-αα′-*dicarboxylic* acid was heated above its melting-point a slight sublimate was noticed, and at the same time carbonic dioxide was apparently given off. Since it seemed probable that the hydride of pyromucic acid might be formed under these conditions a larger portion of the acid was heated to 190° in a stream of hydrogen. Carbonic oxide was formed in abundance and a large crystalline sublimate was obtained. The more volatile portion had condensed in slender needles, but the greater portion was in massive form. The slender needles melted at 128° and after resublimation at 130°. They were formed in such small quantity that a more positive identification of them as pyromucic acid was not possible. The whole crystalline product was therefore dissolved in water and the acid solution neutralized with baric carbonate. The barium salt proved to be very sparingly soluble in water, and no appreciable amount of the readily soluble baric pyromucate could be isolated. The insoluble barium salt, when acidified and extracted with ether, gave the unaltered α-acid melting at 146° (uncorr.) in abundance. A large part of the acid had therefore volatilized without decomposition or isomerization.

---

[1] Ber. d. chem. Ges., **32**, 1040.

On heating the acid in a sealed tube with concentrated hydrochloric or hydrobromic acid we found that carbonization ensued at high temperatures and that at lower temperatures the acid remained unchanged. In alkaline solution the acid is unstable and passes first into the β- and finally into the γ-modification. The details of this isomerization will be more fully discussed in describing the preparation of the latter acids. The prolonged action of sodium amalgam had little effect upon the acid, and the greater part of it could be recovered unchanged.

Oxidation with Nitric Acid and Potassium Permanganate.

The α-acid is readily attacked by oxidizing agents, but we have been able to isolate as products of the oxidation only dehydromucic and oxalic acids. When heated with three times its weight of concentrated nitric acid (sp. gr. 1.42) to 60° a quiet reaction took place which was completed in the course of twelve hours. An insoluble substance had separated which amounted to 13 per cent of the weight of the acid taken. This body sublimed without melting and gave, with ferric chloride, the red jelly characteristic for dehydromucic acid. From the solution could be isolated only oxalic acid, which was identified through its calcium salt and its behavior in a capillary tube. The same products were obtained on treating an alkaline solution of the acid with a sufficient quantity of a 4 per cent solution of potassic permanganate to give 4 atoms of oxygen to each molecule of the acid. The oxidation was allowed to proceed at ordinary temperature, and on acidification of the concentrated alkaline solution dehydromucic acid amounting to 20 per cent of the weight of the α-acid taken was obtained. A careful examination of the solution failed to show the presence of any other product of the reaction except oxalic acid.

Action of Bromine.

When equal molecules of the pure α-acid and bromine were heated in a sealed tube to 140° hydrobromic acid was evolved in abundance and dehydromucic acid was almost the only product. If, however, the acid was exposed to an atmosphere of bromine, it gradually gained in weight, and finally it added rather more than its own weight of bromine. The red transparent mass which was thus obtained was allowed to stand for some time over lime, and then crystallized from chloroform. After repeated recrystallization it melted at 141° (uncorr.) and proved to contain (Analysis V) a percentage of bromine which showed that it was formed by the addition of 1 molecule of bromine to the acid. After recrystallization from water and drying over sulphuric acid the melting-point was raised to 145° (uncorr.). With aqueous bromine a slight oxidation takes place, but the main product is the dibromide of the acid, and it may be prepared most conveniently in this way. The acid is dissolved in twice its weight of water and bromine vapor is slowly passed in by a current of air. When 1 molecule of bromine has thus been added crystals of the dibromide separate in abundance, if the solution is vigorously shaken. The product thus obtained amounts to 50 per cent of the theoretical weight, and from the mother-liquor an additional 10 per cent may be obtained. There remains at last a viscous liquid from which no definite products could be isolated. The nature of this viscous product we have been unable to determine; it is also obtained when the bromine is diluted with anhydrous solvents, or when the vapor of bromine is allowed to act upon the dry acid. From the aqueous solution small amounts of carbonic dioxide were evolved, and occasionally we have also noticed the formation of a small amount of dehydromucic acid. It is worthy of note that this same addition-product was also formed when 2 molecules of bromine were added to an aqueous solution of the potassium salt of the acid.

The product recrystallized from water contained 1 molecule of water, as is shown by the following analyses:

I. 0.2694 gram substance gave 0.2146 gram CO_2; and 0.0585 gram H_2O.

II. 0.1910 gram substance gave 0.2142 gram AgBr.

III. 1.1748 grams substance lost, over sulphuric acid, 0.0641 gram H_2O.

	Calculated for $C_6H_6Br_2O_5.H_2O$.	Found. I.	II.	III.
C	21.43	21.72	....	....
H	2.40	2.42	....	....
Br	47.61	....	47.73	....
H_2O	5.36	....	....	5.46

IV. 0.2090 gram anhydrous substance gave 0.2462 gram AgBr.

V. 0.1586 gram anhydrous substance gave 0.1858 gram AgBr.

	Calculated for $C_6H_6Br_2O_5$.	Found. IV.	V.
Br	50.29	50.14	49.85

The α-dihydrofurfuran-$\alpha\alpha'$-dicarboxylic dibromide is readily soluble in water without essential decomposition and crystallizes in brilliant, four-sided prisms with sharply beveled ends, which melt at 112° to 113° (uncorr.). It is readily soluble in alcohol or in ether, more sparingly soluble in boiling chloroform, from which it crystallizes in rectangular plates. It dissolves very sparingly in hot benzol, and is insoluble in ligroin or carbonic disulphide. The melting-point of the anhydrous body is 147° to 148° (corr.). On treating the aqueous solution with sodium amalgam, or on warming the alcoholic solution with zinc dust the α-acid is reformed. On boiling with water a slow decomposition sets in, accompanied by the escape of carbonic dioxide; in alkaline solution the reaction runs more rapidly.

Action of Baric Hydrate upon α-Dibromide.

The dibromide was dissolved in a little water and 2.5 molecules of baric hydrate were then added. Baric carbonate soon began to separate in the cold, and after standing for twenty-four hours at ordinary temperature the solution was but feebly alkaline. After the removal of the baric carbonate the slight excess of baric hydrate was neutralized with carbonic dioxide and the filtered solution evaporated to a small volume. On cooling, a crystalline salt separated, which was redissolved in a little water and acidified with hydrochloric acid. The highly crystalline acid thus obtained was readily soluble in hot water, contained no trace of bromine, melted at 129° (uncorr.), gave a red-brown precipitate with ferric chloride, and sublimed readily at 100° with the odor of pyromucic acid. The mother-liquor from the baric pyromucate contained baric bromide in abundance. The α-dibromide had therefore been decomposed according to the equation:

$$2C_6H_6Br_2O_5 + 5BaO_2H_2 = (C_5H_3O_3)_2Ba + 2BaCO_3 + 2BaBr_2 + 8H_2O.$$

Careful determination showed that the weight of baric carbonate formed was 92.7 per cent and of the pyromucic acid 92.4 per cent of the amounts demanded by this equation.

Action of Chlorine.

All our attempts to form an addition-product analogous to the bromine derivative just described by the action of dry chlorine upon the α-acid have been unsuccessful. In aqueous solution a crystalline body was easily obtained, but water entered into the reaction, and the product proved to contain hydroxyl as well as chlorine. The pure α-acid was dissolved in twice its weight of water and saturated in the cold with chlorine. On extracting the solution with ether a syrup was obtained which solidified when vigorously stirred. The product may then be purified by recrystallization from a small amount of water. The air-dried substance lost nothing in a desiccator and but a fraction of a milligram when heated for three hours at 125°; at a higher temperature decomposition ensues.

I. 0.2248 gram air-dried substance gave 0.2810 gram CO_2; and 0.0682 gram H_2O.

II. 0.1810 gram air-dried substance gave 0.1242 gram AgCl.

	Calculated for $C_6H_7ClO_6$.	Found. I.	II.
C	34.21	34.10	....
H	3.35	3.39	....
Cl	16.85	....	16.96

This α-chlorhydroxytetrafurfuran-$\alpha\alpha'$-dicarboxylic acid is readily soluble in water and crystallizes in large four-sided prisms with beveled ends. It is readily soluble in alcohol or acetone, more sparingly soluble in ether, and insoluble in ligroin, benzol, chloroform, or carbonic disulphide; it crystallizes well from a mixture of ether and ligroin. The body decomposes at 209° to 210° (corr.). Bromine in aqueous solution seems to have no action upon it, and it is not oxidized by concentrated nitric acid. Acetic anhydride reacts upon it readily and yields a well-crystallized product, which has not yet been further studied.

β-Dihydrofurfuran-$\alpha\alpha'$-dicarboxylic Acid.

The ready isomerization of the α-acid in alkaline solution to the β-modification has already been mentioned, as well as the fact that we have been unable to prepare the α-acid in such a way as to avoid completely this isomerization. The rapidity of the change varies with the temperature and concentration, as also with the nature of the alkaline solution. The preparation of larger quantities of the β-acid is further complicated by its simultaneous partial conversion into the γ-modification. Preliminary experiments showed that the isomerization was but slowly effected by baric hydrate, so that the sparingly soluble barium salt of the α-acid could not conveniently be converted directly into the readily soluble salt of the β-acid; sodic hydrate worked quickly and on the whole was most advantageous. For the isomerization of pure α-acid it was found best to dissolve the acid with an equal weight of sodic hydrate in 20 parts of water, and to boil this solution for an hour with return condenser. Under these conditions about 10 per cent of the α-acid remained unchanged, but not much γ-acid was formed.

The β-acid may be made most conveniently directly from dehydromucic acid by modifying slightly the method of reduction. The dehydromucic acid is suspended in ten times its weight of water and carried into solution by the addition of sodic carbonate ; 30 parts of a 3 per cent sodium amalgam are then added, and the reduction allowed to proceed at ordinary temperature without neutralizing the sodic hydrate formed in the reaction. When all action is over the decanted solution is boiled for a few minutes, acidified, and extracted with ether. The β-acid is then isolated and purified through its sparingly soluble lead salt, as has already been described in explaining the separation and purification of the α-acid. By this process we have obtained directly from dehydromucic acid, 76 per cent of the theoretical yield of pure β-acid. This acid was obtained in a pure condition by Seelig, and we have been able to confirm essentially all his observations. It dissolves in about four times its weight of cold water, much more readily in hot water, and crystallizes from aqueous solution in large, brilliant, complex forms, which contain 1 molecule of water.

I. 0.2091 gram air-dried substance gave 0.3127 gram CO_2; and 0.0878 gram H_2O.

II. 0.5682 gram air-dried substance lost, at 110°, 0.0574 gram H_2O.

	Calculated for $C_6H_6O_5.H_2O$.	Found.	
		I.	II.
C	40.91	40.81	....
H	4.58	4.69	....
H_2O	10.23	....	10.10

The β-dihydrofurfuran-$\alpha\alpha'$-dicarboxylic acid is readily soluble in alcohol, but more sparingly soluble in ether ; it is so much less readily soluble in ether than the α-acid that a partial separation of the two acids is effected in extracting with ether the aqueous solution. It is insoluble in chloroform, benzol, or ligroin, but may be obtained in stout needles from solution in a mixture of ether and ligroin. The anhydrous acid melts at 178° to 179° (corr.) ; the hydrous acid collapses with the loss of water above 100°.

In addition to the barium, calcium, and silver salts, which were investigated by Seelig, we have studied also the lead salt.

Baric α-Dihydrofurfuran-αα'-dicarboxylate, $BaC_6H_4O_5.1\frac{1}{2}H_2O$.—A hot concentrated solution of the acid was neutralized with baric hydrate, the mother-liquor drained from the salt which separated on cooling, and the solid well washed with cold water. The air-dried salt then had the composition assigned to it by Seelig.

0.6853 gram air-dried salt lost, at 185°, 0.0600 gram H_2O.

	Calculated for $BaC_6H_4O_5.1\frac{1}{2}H_2O$.	Found.
H_2O	8.43	8.76

0.1996 gram anhydrous salt gave 0.1574 gram $BaSO_4$.

	Calculated for $BaC_6H_4O_5$.	Found.
Ba	46.82	46.40

The solubility of the salt in cold water was also determined.

6.877 grams of solution saturated at 20° gave 0.0766 gram BaSO4.

Hence the aqueous solution saturated at 20° contained 1.40 per cent of the anhydrous salt.

Calcic β-dihydrofurfuran-αα'-dicarboxylate, $CaC_6H_4O_5.2\frac{1}{2}H_2O$.—This salt, prepared by neutralizing an aqueous solution of the acid with calcic carbonate, was very readily soluble in water, and a hot concentrated solution gelatinized on cooling. The gelatinous mass, on exposure to the air, gave a permanent, solid salt which apparently contained 2.5 molecules of water. Seelig prepared a salt by precipitating the aqueous solution with alcohol, which contained 1.5 molecules.

I. 0.2229 gram air-dried salt gave 0.1251 gram $CaSO_4$.

II. 0.9922 gram air-dried salt lost, at 200°, 0.1794 gram H_2O.

	Calculated for $CaC_6H_4O_5.2\frac{1}{2}H_2O$.	Found.	
		I.	II.
Ca	16.59	16.50	....
H_2O	18.68	....	18.08

0.2150 gram anhydrous salt gave 0.1468 gram $CaSO_4$.

	Calculated for. $CaC_6H_4O_5$.	Found.
Ca	20.40	20.07

Argentic β-Dihydrofurfuran-αα′-dicarboxylate, $Ag_2C_6H_4O_5$.—The silver salt crystallizes in microscopic needles which are not very sparingly soluble in cold water, but the solubility is not much increased by heat.

0.2025 gram air-dried salt gave 0.1562 gram AgCl.

	Calculated for $Ag_2C_6H_4O_5$.	Found.
Ag	58.03	58.05

Plumbic β-Dihydrofurfuran-αα′-dicarboxylate, $PbC_6H_4O_5.H_2O$.—This salt was prepared for analysis by precipitating with plumbic nitrate a solution of the ammonium salt of the acid. The air-dried salt contained 1 molecule of water, one-half of which is lost at 195°; at higher temperature decomposition sets in. From boiling water it was deposited in small, clear, rhombic plates.

I. 0.1849 gram air-dried salt gave 0.1463 gram $PbSO_4$.

II. 0.2510 gram air-dried salt gave 0.1993 gram $PbSO_4$.

III. 1.0127 grams air-dried salt lost, at 195°, 0.0235 gram H_2O.

IV. 0.9390 gram air-dried salt lost, at 195°, 0.0213 gram H_2O.

	Calculated for $PbC_6H_4O_5.H_2O$.	Found.			
		I.	II.	III.	IV.
Pb	54.31	54.05	54.24	....	....
$\frac{1}{2}H_2O$	2.36	....	....	2.32	2.27

The solubility of the salt in hot and cold water was also determined by the methods used in the case of the lead salt of the α-acid.

I. 87.51 grams solution, saturated at 20°, gave 0.0085 gram $PbSO_4$.

II. 96.76 grams solution, saturated at 20°, gave 0.0109 gram $PbSO_4$.

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.012	0.013

I. 54.88 grams solution, saturated at 99°.5, gave 0.0152 gram $PbSO_4$.

II. 59.41 grams solution, saturated at 99°.5, gave 0.0111 gram $PbSO_4$.

The solution saturated at 99°.5 therefore contained the following percentages of the anhydrous salt :

I.	II.
0.032	0.022

On heating the β-dihydrofurfuran-αα′-dicarboxylic acid with fuming hydrobromic acid to 100° we found that it remained unchanged, while at 150° carbonization ensued. A 10 per cent solution of the acid was treated with a large excess of sodium amalgam, but nearly the whole amount taken was recovered unchanged. On long boiling with a solution of sodic hydrate the acid was completely isomerized into the γ-modification which is described later.

Oxidation with Nitric Acid and Potassic Permanganate.

Concentrated nitric acid (sp. gr. 1.42) oxidizes the β-acid readily at 100°; we found that the reaction ran quietly, and at the end of three hours was apparently complete. Dehydromucic acid, amounting to about 20 per cent of the weight of the β-acid taken, had then separated and was fully identified by its behavior in a capillary tube and its reaction with ferric chloride. From the mother-liquor nothing but oxalic acid could be isolated. Permanganate in alkaline solution was immediately decolorized, but after the addition of a sufficient quantity to give 4 atoms of oxygen to each molecule of the acid, nothing but oxalic acid could be isolated from the concentrated solution. If dehydromucic acid was formed in the reaction it was only in insignificant quantity.

Action of Bromine.

When exposed to the vapor of bromine at ordinary temperature the acid slowly gained in weight, but after three days this gain amounted to but 28 per cent of that required by the addition of one molecule of bromine, and a part of this was again lost on standing over lime. At 140°, in a sealed tube, an addition-product was formed, but at the same time a certain amount of hydrobromic acid was evolved and small quantities of dehydromucic acid could be detected. Dilution with chloroform gave no satisfactory results, but the addition-product could easily be formed in aqueous solution. Bromine vapor was passed into a saturated aqueous solution of the acid by means of a current of air; the color of the bromine rapidly disappeared, and when 1 molecule had been taken up a crystalline precipitate separated spontaneously or after shaking the solution. The product may then be crystallized from water and forms four-sided, obliquely truncated prisms which contain 2 molecules of water.

I. 0.1865 gram air-dried substance gave 0.1974 gram AgBr.

II. 0.7475 gram air-dried substance lost, at 105°, 0.0750 gram H_2O.

	Calculated for $C_6H_6Br_2O_5.2H_2O$.	Found.	
		I.	II.
Br	45.17	45.05	....
H_2O	10.18	....	10.03

0.2018 gram anhydrous substance gave 0.2389 gram AgBr.

	Calculated for $C_6H_6Br_2O_5$.	Found.
Br	50.29	50.40

The β-dihydrofurfuran-$\alpha\alpha'$-dicarboxylic dibromide is readily soluble in alcohol or ether, but slightly soluble in hot benzol or chloroform, and is insoluble in ligroin or carbonic disulphide. In a capillary tube it decomposes at 213° to 214° (corr.). Sodium amalgam reduces it readily to the β-acid. On boiling the aqueous solution a slow decomposition sets in; apparently the same decomposition takes place rapidly in alkaline solution.

Action of Baric Hydrate on β-Dibromide.

To a cold aqueous solution of the β-dibromide was added 2.5 molecules of baric hydrate. After standing for thirty-six hours the feebly alkaline solution was filtered from the baric carbonate which had separated, the slight excess of baric hydrate removed with carbonic dioxide, and the clear solution evaporated to a small volume. The crystalline barium salt which was obtained as the solution cooled gave, on acidification, an abundant separation of pyromucic acid, which melted at 130° (uncorr.), sublimed readily at 100°, and gave a red-brown precipitate with ferric chloride. Baric bromide had also been formed in abundance. The reaction was therefore identical with that which he had observed in the case of the corresponding α-compound.

$$2C_6H_6Br_2O_5 + 5BaO_2H_2 = (C_5H_3O_3)_2Ba + 2BaCO_3 + 2BaBr_2 + 8H_2O.$$

The weight of the baric carbonate formed was 90 per cent and that of the baric pyromucate 88.5 per cent of the amount required by this equation.

Action of Chlorine.

The β-acid was dissolved in four times its weight of water, the solution cooled with ice, and saturated with chlorine. On extraction with ether a thick syrup was obtained, which solidified on stirring. The body may then be crystallized from a small amount of water or from ether. It forms large, obliquely truncated prisms, which melt at 95° and contain 1.5 molecules of water. The yield amounts to about 33 per cent of the weight of the β-acid taken.

0.9201 gram air-dried substance lost, over sulphuric acid, 0.1041 gram H_2O.

	Calculated for $C_6H_7ClO_6.1\frac{1}{2}H_2O$.	Found.
H_2O	11.38	11.32

0.2031 gram substance, dried over sulphuric acid, gave 0.1408 gram AgCl.

	Calculated for $C_6H_7ClO_6$.	Found.
Cl	16.85	17.14

Like the corresponding derivative of the α-acid this body reacts with acetic anhydride and forms a crystalline product, which has not been further studied.

γ-Dihydrofurfuran-αα'-Dicarboxylic Acid.

In studying the formation of the β-acid it soon became evident that the yield of this acid was greatly diminished, if the action of the sodic hydrate was carried too far. At first we assumed that this loss was due to the formation of products of a radically different nature; but when we discovered that the α- and β-acids were merely stereometrically different forms of the same structure, and that the difference between them was not conditioned by an alteration in the position of the double bond, we determined to push the reaction to its limit. Pure α-acid was accordingly dissolved in ten times its weight of water, and twice its weight of sodic hydrate was added; the solution was then heated upon the water-bath for sixteen hours in a silver flask, the solution acidified and extracted with ether in the apparatus already described. In a short time a crystalline acid, very sparingly soluble in ether, began to separate in the flask, and when the extraction was complete the weight of the new acid obtained was substantially equal to that of the α-acid taken. Analysis showed that this was a third or γ-modification of the dihydrofurfuran-αα′-dicarboxylic acid. Its preparation in quantity, directly from dehydromucic acid, was a simple matter. A solution of sodic dehydromucate, containing 10 per cent of the acid, was reduced at ordinary temperature with finely divided 3 per cent sodium amalgam; 30 grams of the amalgam were used for each gram of the acid. After twenty-four hours the strongly alkaline solution was decanted from the mercury, filtered, and boiled for sixteen hours in a silver flask fitted with a return cooler. The solution was then acidified and thoroughly extracted with ether. In this way 84 per cent of the theoretical yield of crude acid may be obtained, and it is so sparingly soluble even in boiling ether that its purification is a matter of no difficulty. For analysis it was further recrystallized several times from water. The air-dried acid lost nothing in weight over sulphuric acid.

0.2114 gram substance gave 0.3528 gram CO_2; and 0.0726 gram H_2O.

	Calculated for $C_6H_6O_5$.	Found.
C	45.55	45.52
H	3.83	3.84

The γ-acid is readily soluble in cold water and crystallizes from warm aqueous solution in stellate clusters of plates. It dissolves readily in alcohol, but requires nearly 200 parts of boiling ether for its solution; hot glacial acetic acid dissolves it freely, but the greater part is again deposited on cooling; it is insoluble in chloroform, ligroin, or benzol. In a capillary tube the acid decomposes without melting, but the temperature varies greatly with the time; at 170° the time required was found to be eleven minutes, while ten seconds sufficed at 210°. If the substance was introduced into the bath and the temperature raised at the usual rate, decomposition took place at about 194° (uncorr.). As the decomposition was attended by the escape of carbonic dioxide a determination of the amount thus given off was made. It was found, however, that the total loss in weight at 170° was but 9.51 per cent and that a part of this, 2.20 per cent, was due to the formation of water, while a loss of 27.84 per cent was required by the formation of 1 molecule of carbonic dioxide.

The γ-acid was discovered toward the end of our investigation, and we have been unable as yet to make a systematic study of its salts. We have been obliged to content ourselves with the study of its reduction and oxidation, and the product formed from it by the addition of bromine.

Action of Sodium Amalgam.

While the α- and β-acids are not affected by nascent hydrogen the γ-acid is reduced in alkaline solution, although a large excess of sodium amalgam seems to be necessary to complete the reaction. The products formed are two stereoisomeric forms of the tetrahydrofurfuran-$\alpha\alpha$-dicarboxylic acid, which were recently described by Lean.[1] We had just succeeded in isolating these two acids by a method quite different from Lean's when his paper reached us. Our own observations agreed so closely with the description of his results that we thought it unnecessary to carry our investigations further.

The γ-acid was dissolved in twenty times its weight of water and neutralized with sodic carbonate; 125 grams of a 3 per cent sodium amalgam were then added for each gram of the acid, the mixture heated upon a water-bath, and a rapid stream of carbonic dioxide passed into the solution. When the action was over, the liquid was acidified and extracted with ether. The viscous product obtained gradually solidified, but gave no indication of a definite melting-point. It was therefore dissolved in two hundred times its weight of water and the boiling solution neutralized with plumbic carbonate. The filtered solution proved to contain the whole of the lead salts formed, and as concentration failed to cause the separation of any noticeable quantity of salt it was evaporated to dryness. The residue consisted of white, opaque crystals embedded in a transparent varnish. On the addition of a little cold water the whole mass grew opaque and increased considerably in bulk. It was then found that the salt was no longer readily soluble in water, but that little more than 0.5 of it was dissolved by 70 parts of boiling water. The soluble and insoluble portions were therefore separately acidified and extracted with ether. From the insoluble portion an acid was obtained which was indifferent to bromine and which melted completely, though not sharply, at 95°. After recrystallization from water it melted at 59° to 61°, and on dehydration over sulphuric acid the melting-point again rose to 94° to 95°. The acid was readily soluble in water or alcohol, more sparingly soluble in ether, and insoluble in chloroform, ligroin, or benzol. It could easily be recrystallized from concentrated hydrochloric acid as recommended by Lean. These properties sufficiently identify it as one of the tetrahydrofurfuran-$\alpha\alpha'$-dicarboxylic acids described by Lean. The acid obtained from the soluble lead salt melted at 115° to 116°, but this melting-point was easily raised to 124° by recrystallization from a mixture of ether and ligroin. It was readily soluble in water, alcohol, or glacial acetic acid, more sparingly soluble in ether, and insoluble in chloroform, ligroin, or benzol. From boiling toluol it crystallized in leafy aggregations. This acid agrees with the description given by Lean of the second form of his tetrahydrofurfuran-$\alpha\alpha'$-dicarboxylic acid.

---

[1] J. Chem. Soc., 77, 103.

Oxidation with Nitric Acid and Potassic Permanganate.

The γ-acid was much more readily attacked by nitric acid than either the α- or the β-acid; even a diluted acid (sp. gr. 1.25) reacted vigorously at 100°. The products formed proved to be oxalic acid and a small amount of dehydromucic acid. These two acids were also formed by oxidation with permanganate in alkaline solution, although the amount of dehydromucic acid obtained was extremely small.

Action of Bromine.

The γ-acid is readily attacked by bromine, but we have been unable to prepare in a pure condition the addition-product which is formed. Little or no crystalline product could be obtained either by exposure to bromine vapor or by adding bromine to an aqueous solution of the acid. Preliminary experiments showed that chloroform was the only anhydrous diluent that promised to give satisfactory results, and in this case the insolubility both of the acid and its dibromide made its use inconvenient or impracticable. By the addition of a small amount of glacial acetic acid this difficulty was obviated, but the product which we obtained contained too small a percentage of bromine. As the evolution of hydrobromic acid was always noticed the product doubtless contained an admixture of the corresponding substituted acid. The most successful preparations were made as follows: 15 grams of dry chloroform were mixed with 2.5 grams of glacial acetic acid (99.5 per cent) and 1 gram of bromine; 1 gram of pure γ-acid was then added, the mixture shaken thoroughly, and the solution quickly filtered from the small amount of unaltered γ-acid; the separation of prismatic crystals of the dibromide begins at once and the separation is soon complete. The crude product, which amounts to 50 per cent of the theoretical yield, is then purified by washing with boiling benzol, to which a few drops of pure acetone have been added. The substance may also be recrystallized from a mixture of ether and ligroin, and the material used in Analysis III was thus prepared.

I. 0.1802 gram substance gave 0.2058 gram AgBr.
II. 0.2009 gram substance gave 0.2306 gram AgBr.
III. 0.1244 gram substance gave 0.1419 gram AgBr.

	Calculated for $C_6H_6Br_2O_6$.	Found.		
		I.	II.	III.
Br	50.29	48.61	48.85	48.54

This body is readily soluble in water or alcohol with apparent decomposition, more sparingly soluble in ether, and insoluble in chloroform, ligroin, or benzol. The purified substance decomposes slowly on standing, and is still more unstable in solution. The decomposition of the solid becomes more rapid at higher temperature, and at about 200° it is immediate.

Action of Baric Hydrate on γ-Dibromide.

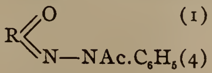
Although the γ-dibromide could not be obtained in a pure condition our analyses made it evident that it was the main constituent of the product which we had prepared; we therefore thought it worth while to try its behavior with baric hydrate. We have satisfied ourselves that no baric pyromucate is formed in the reaction, but we have not yet been able to study the products of the decomposition in detail. When 2.5 molecules of baric hydrate were added to an aqueous solution of the substance a precipitate was formed at once, and in a short time the solution gave a neutral reaction. The barium salt which separated proved to contain baric carbonate in abundance, but a considerable portion of it was soluble in boiling water. The acid set free from this salt could be extracted by ether, but remained as an uncrystallizable syrup on evaporation of the ether. The only soluble barium salt formed in the reaction appeared to be baric bromide, and no trace of pyromucic acid could be detected.

THE CONSTITUTION OF THE OXYAZO COMPOUNDS.

By William McPherson and Herbert C. Gore.

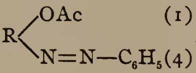
In a previous article published in this Journal[1] results were given which absolutely proved the constitution of the acyl derivatives of the paraoxyazo compounds. The problem was to decide between the two possible formulæ:

I.



$$R\left\langle\begin{matrix} =O \quad (1) \\ =N-NAc.C_6H_5(4) \end{matrix}\right.$$

and II.

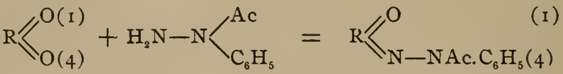


$$R\left\langle\begin{matrix} -OAc \quad (1) \\ -N=N-C_6H_5(4) \end{matrix}\right..$$

---

[1] Vol. **22**, 364.

The proof was found in the synthesis of bodies having beyond doubt the constitution represented by Formula I. This synthesis was effected by the interaction of unsymmetrical acylphenylhydrazines and paraquinones according to the general reaction :



$$R{<}\begin{matrix}O(1)\\O(4)\end{matrix} + H_2N{-}N{<}\begin{matrix}Ac\\C_6H_5\end{matrix} = R{<}\begin{matrix}O & & (1)\\N{-}NAc.C_6H_5 & & (4)\end{matrix}$$

On comparing these hydrazone derivatives with the same derivatives of the corresponding oxyazo bodies, they were found to be not identical but isomeric. Hence the constitution of the acyl derivatives of the paraoxyazo bodies must be expressed by Formula II. In other words, they are true oxyazo compounds containing the acyl group joined to oxygen.

While this proof does not fix the constitution of the free oxyazo compounds, nevertheless the reactions bear indirectly upon the subject, and certain reasons were given for considering them, as well as their salts, true oxyazo bodies. One of these reasons, *viz.*, that the free paraoxyazo bodies cannot be quinone derivatives since they do not react with phenylhydrazine, must, however, be withdrawn, as I have found that under certain conditions a reaction does take place.[1] This reaction is being studied and it is hoped that it may throw some light on the constitution of these bodies.

Since the above-mentioned article was published, Farmer and Hantzsch[2] have published the results of the measurements of the electrical conductivity of oxyazobenzene as well as of its sodium salt, and conclude that while the latter is a true oxyazo body the former is benzoquinonephenylhydrazone. The publication of these results was soon followed by an article by Auwers,[3] giving the results of cryoscopic measurements, which he believes prove that the paraoxyazo compounds are, in a free state, true oxyazo bodies, although the orthooxyazo compounds are quinone hydrazones. More recently Möhlau and Kegel,[4] from a study of the condensation-products of certain paraoxyazo bodies with tetramethyldiamidobenzhydrol, conclude that the view of Farmer and Hantzsch is correct.

---

[1] See note, this Journal, Vol. 25, 80.

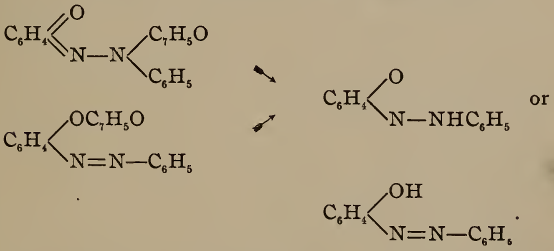
[2] Ber. d. chem. Ges., **32**, 3089.

[3] *Ibid.*, **33**, 1302.

[4] *Ibid.*, **33**, 2858.

It will be noted that it is only the constitution of the free paraoxyazo compounds which remains unsettled. It is generally accepted that the salts, as well as the acyl and alkyl derivatives of these, are true oxyazo bodies. In the case of the members of the ortho series, all evidence goes to show that they are quinone hydrazones.

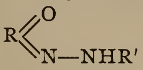
In the article[1] referred to above I have shown that both the acyl derivatives of the quinone hydrazones and their isomeric paraoxyazo derivatives give, on saponification, the same body. Thus quinone benzoylphenylhydrazone and its isomeric benzoyl derivative of oxyazobenzene give, on saponification with acids and alkalies, the same body; *viz.*, oxyazobenzene:



$$C_6H_4\begin{cases}O\\ N-N\begin{cases}C_7H_5O\\ C_6H_5\end{cases}\end{cases} \searrow \qquad C_6H_4\begin{cases}O\\ N-NHC_6H_5\end{cases} \text{ or }$$

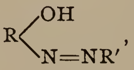
$$C_6H_4\begin{cases}OC_7H_5O\\ N=N-C_6H_5\end{cases} \nearrow \qquad C_6H_4\begin{cases}OH\\ N=N-C_6H_5\end{cases}.$$

The investigation has been continued in the hope that some compound could be found which, on saponification, would give the two possible isomers



$$R\begin{cases}O\\ N-NHR'\end{cases}$$

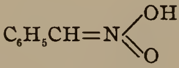
and



$$R\begin{cases}OH\\ N=NR'\end{cases},$$

just as Hantzsch and Schultze[2] have been able to obtain from the sodium salt of phenylnitromethane by treatment with acids the two isomers

$C_6H_5CH_2NO_2$ and



$$C_6H_5CH=N\begin{cases}OH\\ O\end{cases}.$$

---

[1] This Journal, **22**, 364.

[2] Ber. d. chem. Ges., **29**, 699.

Accordingly, the action of the unsymmetrical benzoyl-α-naphthylhydrazine on the paraquinones has been studied; and while the saponification of these has not led to the isolation of such isomeric bodies, yet the results are of sufficient interest to make their publication desirable. They show that the acyl derivatives of the paraoxyazo bodies formed by the interaction of α-naphthyl diazonium chloride on phenol, orthocresol, and thymol, respectively, contain the acyl group joined to oxygen and hence are true oxyazo compounds.

EXPERIMENTAL PART.

I. The Preparation of α-Benzoyl-α-Naphthylhydrazine, $C_{10}H_7.NC_7H_5O.NH_2$.

This compound was prepared according to Widman's method[1] for the preparation of unsymmetrical hydrazines. To 1 gram of β-acetylnaphthylhydrazine (m. p. 143°) dissolved in 10 cc. of benzene was added the theoretical amount of benzoyl chloride. The flask was connected with a return condenser and the solution boiled until the evolution of hydrochloric acid ceased. This required about one hour. On evaporating the benzene, a thick, gummy liquid remained, which was dissolved in as little alcohol as possible. On scratching the sides of the beaker containing the solution with a glass rod, white crystals of α-benzoyl-β-acetyl-α-naphthylhydrazine separated. Yield, 0.84 gram. By further crystallization from alcohol the pure body, melting at 184°, was obtained.

0.2046 gram substance gave 0.5603 gram CO_2; and 0.0967 gram H_2O.

0.2062 gram substance gave 0.1017 gram H_2O.

0.3010 gram substance gave 26.5 cc. N at 25° and 741 mm.

	Calculated for $C_{19}H_{16}N_2O_2$.	Found.	
		I.	II.
C	75.00	74.69	....
H	5.26	5.25	5.48
N	9.21	9.62	....

---

[1] Monograph—"Ueber asymmetrische Secundäre Phenylhydrazine" published by the "Gesellschaft der Wissenschaften" at Upsala, 1893; also Ber. d. chem Ges., **26**, 945.

The pure compound is fairly soluble in hot alcohol, from which it is deposited in large, lath-shaped crystals. It is slightly soluble in benzene and benzene-ligroin, being deposited from the latter in little nodules of microscopic crystals. By treatment with dilute sulphuric acid it is converted into *α*-benzoyl-*α*-naphthylhydrazine. To effect this change a solution of 2 cc. of sulphuric acid, in 15 cc. of water, was added to 2 grams of the hydrazine. The mixture was heated and sufficient alcohol added to form a clear solution. The flask was then connected with a return condenser and the contents kept at a boiling temperature for about four hours, or until the odor of benzoic ether was detected. The cooled solution was then neutralized with sodium carbonate and extracted with ether, which, on evaporation, deposited white crystals of the unsymmetrical benzoyl-*α*-naphthylhydrazine. By repeated crystallization from alcohol the pure body melting at 120°.5 was obtained :

0.2058 gram substance gave 0.5854 gram CO_2 ; and 0.1070 gram H_2O.

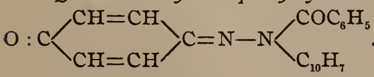
0.2032 gram substance gave 20 cc. N at 23° and 744.3 mm.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.58
H	5.34	5.77
N	10.68	10.91

α-Benzoylnaphthylhydrazine is very soluble in alcohol and benzene. It is deposited from its alcoholic solution in large truncated pyramids. On addition of ligroin to its benzene solution, feathery crystals, melting at 98°, are deposited. On gentle heating or on long standing in a vacuum the melting-point gradually rises to 120°.5.

II. The Action of α-Benzoyl-α-naphthylhydrazine on Paraquinones of the Benzene Series.

a. Quinonebenzoyl-α-naphthylhydrazone,



$$O:C\left\langle\begin{matrix}CH=CH\\CH=CH\end{matrix}\right\rangle C=N-N\left\langle\begin{matrix}COC_6H_5\\C_{10}H_7\end{matrix}\right.$$

.—A solution of 1 gram of benzoquinone in 15 cc. of alcohol was poured into 500 cc. of water. To this was added 2 grams of *α*-benzoyl-*α*-naphthylhydrazine dissolved in 200 cc. of water and 50 cc. of alcohol. The addition of a few drops of hydrochloric acid accelerates the reaction. The yellow hydrazone at once began to separate. After half an hour the precipitate was collected by stirring, filtered off and dried on a clay plate. 2.2 grams of the impure body were obtained. The hydrazone is difficult to purify on account of its tendency to separate from its solution in the form of an oil. It is very soluble in benzene, alcohol, ether, and chloroform, separating from each as an oil that does not solidify. On heating the oil with successive portions of ligroin, however, a solution was obtained from which the hydrazone was deposited as a crust on the sides of the beaker. On standing for two or three days a few large crystals were formed which were removed and washed with ligroin. By further purification from ligroin a small amount of the body was obtained in masses of plates, melting sharply at 113°.5.

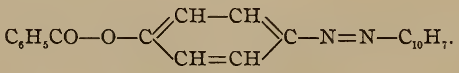
0.2238 gram substance gave 0.6484 gram CO_2; and 0.0961 gram H_2O.

0.2258 gram substance gave 17.6 cc. N at 31°.5 and 738.8 mm.

	Calculated for $C_{23}H_{16}N_2O_2$.	Found.
C	78.41	79.015
H	4.54	4.77
N	7.95	8.22

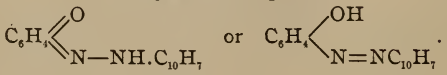
The percentage of carbon found is too high, but the difficulty experienced in obtaining the pure material prevented our making another combustion.

Quinone benzoyl-α-naphthylhydrazone is isomeric with the benzoyl derivative of α-naphthaleneazophenol. The latter must therefore have the formula :



On saponification both of these compounds yield the same body, *viz.* :

α-Naphthaleneazophenol,



This compound can be readily prepared by the interaction of α-naphthyl diazonium chloride and phenol. 7.7 grams of α-naphthylamine were ground in a mortar with a hydrochloric acid solution corresponding to 3.9 grams of the anhydrous acid. The resulting product was added to 200 cc. of water, cooled to 5°, and diazotized with the required amount of sodium nitrite dissolved in 100 cc. of water. The solution was then filtered and added to a cold solution of sodium phenolate, prepared by adding 5 grams of phenol and 2.4 grams of sodium hydroxide to a liter of water. After standing twenty-four hours the azo compound was precipitated by hydrochloric acid and purified by repeated crystallization from benzene-ligroin (m. p. 136°).

0.2016 gram substance gave 0.5708 gram CO_2; and 0.0954 gram H_2O.

0.2062 gram substance gave 0.0944 gram H_2O.

0.2045 gram substance gave 21.8 cc. N at 26°.5 and 740.8 mm.

	Calculated for $C_{16}H_{12}N_2O$.	Found.	
		I.	II.
C	77.42	77.22	....
H	4.84	5.26	5.09
N	11.29	11.56	....

α-Naphthaleneazophenol is easily soluble in alcohol, separating in little clumps of brownish needles. From benzene it separates in yellowish needles. It is slightly soluble in ligroin, separating in brownish plates. When these are heated to 130° the color suddenly changes to red. This red modification is deposited from its ligroin solution in the form of reddish silky needles. The distinction between the two modifications is thus very marked. The experiments of Hewitt[1] pointed to the presence of water in the brown body; but experiments showed that the change from the brown to the red modification was not attended by any change in weight. It is possible that we have here the two isomers

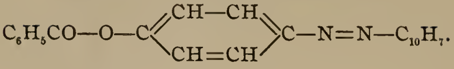
$$C_{10}H_7N = N—C_6H_4OH \text{ and } C_{10}H_7NH—N = C_6H_4 = O,$$

but no evidence could be obtained of any difference in chemical behavior.

---

[1] Ber. d. chem. Ges., 28, 799.

Benzoate of α-Naphthaleneazophenol,



$$C_6H_5CO{-}O{-}C\left\langle\begin{matrix}CH{-}CH\\CH{=}CH\end{matrix}\right\rangle C{-}N{=}N{-}C_{10}H_7.$$

This compound was readily obtained from naphthaleneazophenol by means of Baumann's reaction. By precipitating its benzene solution with ligroin, the pure body was obtained melting at 120°.

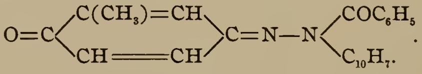
0.2015 gram substance gave 0.5801 gram CO_2; and 0.0794 gram H_2O.

0.2154 gram substance gave 16.35 cc. N at 29° and 749.8 mm.

	Calculated for $C_{23}H_{16}N_2O_2$.	Found.
C	78.41	78.515
H	4.54	4.38
N	7.95	8.23

The compound is readily soluble in chloroform and benzene and fairly so in ether and alcohol. It is deposited in the form of needles from its solution in each of these solvents.

b. Toluquinonebenzoyl-α-naphthylhydrazone,



$$O{=}C\left\langle\begin{matrix}C(CH_3){=}CH\\CH{=}CH\end{matrix}\right\rangle C{=}N{-}N\left\langle\begin{matrix}COC_6H_5\\C_{10}H_7.\end{matrix}\right.$$

3.8 grams of toluquinone were dissolved in 100 cc. of alcohol and the solution poured into 800 cc. of water. To this was added a solution of 9 grams of α-benzoyl-α-naphthylhydrazine hydrochloride dissolved in 400 cc. of dilute alcohol (equal volumes of alcohol and water). The resulting mixture was allowed to stand over night when the hydrazone was collected by stirring and removed by filtration. (Yield of impure compound 8.5 grams.) Like the corresponding derivative of benzoquinone, the impure compound is deposited from the common solvents as an oil. It was finally obtained in the form of crystals by repeated treatment with small amounts of hot methyl alcohol, which dissolved principally the resinous matter. The residue left was bright-yellow. This was then deposited from benzene-ligroin in clusters of stellar crystals. The pure compound melts at 166°.

0.2012 gram substance gave 0.5812 gram CO_2; and 0.0953 gram H_2O.

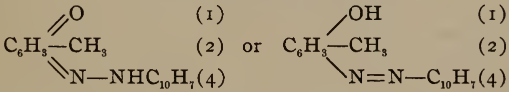
0.2509 gram substance gave 17.8 cc. N at 19°.5 and 737.3 mm.

	Calculated for $C_{24}H_{18}N_2O_2$.	Found.
C	78.69	78.78
H	4.91	5.26
N	7.65	7.92

From alcohol the pure hydrazone crystallizes either in broad prismatic crystals with pyramidal ends or in squares.

The compound is not identical but isomeric with the benzoate of α-naphthaleneazoorthocresol. The latter must therefore be a true oxyazo compound containing the benzoyl group joined to oxygen. Both of these compounds yield, on saponification,

α-*Naphthaleneazoorthocresol*,



This compound can be readily prepared by the interaction of α-naphthyl diazonium chloride and orthocresol. The following conditions were found by Mr. C. P. Linville, of this laboratory, to give good results: 10.5 grams of α-naphthylamine were triturated in a mortar with a solution of hydrochloric acid containing 5.36 grams of the anhydrous acid. 350 cc. of water were added and the compound diazotized at 5° by the addition of a cold solution of 5.5 grams of sodium nitrite in 100 cc. of water. The resulting diazonaphthalene solution, filtered from the residue, was gradually added to a cold solution of 8 grams of orthocresol and 3 grams of sodium hydroxide in 1500 cc. of water. The α-naphthaleneazocresol separated as a yellow precipitate. Yield of crude product 12 grams. It can easily be purified by benzene-ligroin. Melting-point 154°.5.

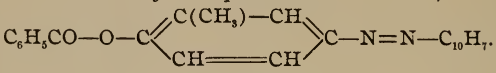
0.2000 gram substance gave 0.5713 gram CO_2; and 0.1018 gram H_2O.

0.2000 gram substance gave 19.2 cc. N at 20° and 744 mm.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.90
H	5.34	5.65
N	10.68	10.79

The compound is very soluble in alcohol and benzene. From the latter it separates in reddish-yellow needles and ball-shaped masses.

Benzoate of α-Naphthaleneazoorthocresol,



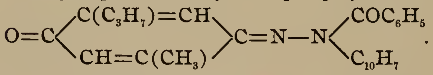
To obtain this the α-naphthaleneazocresol was dissolved in a 10 per cent solution of sodium hydroxide and the resulting solution shaken up with a slight excess of benzoyl chloride. The compound was purified by crystallization, first from alcohol and then from ligroin, from which it separates in long, thin, flat needles. Melting-point 120°.

0.2000 gram substance gave 0.5763 gram CO_2; and 0.0943 gram H_2O.

0.2000 gram substance gave 14.6 cc. N at 25° and 743 mm.

	Calculated for $C_{24}H_{18}N_2O_2$.	Found.
C	78.68	78.58
H	4.92	5.24
N	7.65	8.005

c. Thymoquinonebenzoyl-α-naphthylhydrazone,



3.13 grams of thymoquinone were dissolved in 200 cc. of alcohol and the solution poured into 400 cc. of cold water. To this was added a solution of 5 grams of α-benzoyl-α-naphthylhydrazine hydrochloride in 320 cc. of dilute alcohol (equal parts of alcohol and water). After standing for twenty-four hours, the hydrazone separated in beautiful yellow crystalline groups. Yield 5 grams. On crystallizing from benzene-ligroin the pure body was obtained, melting at 151°.5.

0.2009 gram substance gave 0.5860 gram CO_2; and 0.1095 gram H_2O.

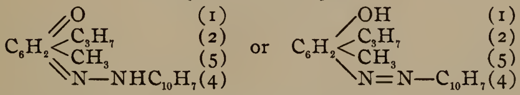
0.2605 gram substance gave 16.4 cc. N at 16°.5 and 728 mm.

	Calculated for $C_{27}H_{24}N_2O_2$.	Found.
C	79.41	79.55
H	5.88	6.06
N	6.86	7.04

The hydrazone crystallizes from alcohol in beautiful rhombohedral crystals and from benzene-ligroin in compact bladed aggregates.

Thymoquinone benzoyl-α-naphthylhydrazone, on saponification, yields α-naphthaleneazothymol. On benzoylating this body, however, we obtain not the original hydrazone but the isomeric benzoate of α-naphthaleneazothymol, which body must therefore contain the benzoyl group joined to oxygen.

α-Naphthaleneazothymol,[1]



$$C_6H_2\left\langle\begin{array}{ll} =O & (1) \\ -C_3H_7 & (2) \\ -CH_3 & (5) \\ =N-NHC_{10}H_7 & (4) \end{array}\right. \quad \text{or} \quad C_6H_2\left\langle\begin{array}{ll} -OH & (1) \\ -C_3H_7 & (2) \\ -CH_3 & (5) \\ -N=N-C_{10}H_7 & (4) \end{array}\right.$$

The α-naphthaleneazothymol so prepared is identical with that obtained by the ordinary method of preparing oxyazo bodies. Mr. W. L. Dubois, of this laboratory, obtained a yield of 78 per cent under the following conditions: 7.7 grams of finely powdered α-naphthylamine were suspended in 200 cc. of water, to which had been added a solution of hydrochloric acid corresponding to 3.9 grams of the anhydrous acid. This was cooled, diazotized with sodium nitrite, filtered, and the resulting solution of the α-naphthyl diazonium chloride added slowly to a cold solution of 8.07 grams of thymol and 2.6 grams of sodium hydroxide in 1000 cc. of water. The yellowish-brown α-naphthaleneazothymol separated as fast as formed. From benzene-ligroin it separates in monoclinic crystals melting at 117°.5.

0.2009 gram substance gave 0.5820 gram CO_2; and 0.1246 gram H_2O.

0.2005 gram substance gave 16.9 cc. N at 23° and 740 mm.

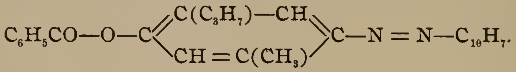
---

[1] The melting-point of the corresponding benzeneazothymol is given by Mazzara and Possetto (Gazz. chim. ital., **15**, 52-228) as 85° to 90°. The melting-point is not raised above this by repeated crystallization from alcohol. By a single crystallization from benzene, however, the melting-point is raised to 109° and remains constant.

	Calculated for $C_{20}H_{20}N_2O$.	Found.
C	78.95	79.01
H	6.58	6.89
N	9.21	9.295

The compound is very soluble in ether and benzene and fairly so in alcohol.

Benzoate of α-Napthaleneazothymol,



$$C_6H_5CO{-}O{-}C\left\langle\begin{matrix}C(C_3H_7){-}CH\\CH=C(CH_3)\end{matrix}\right\rangle C{-}N=N{-}C_{10}H_7.$$

This compound is obtained from α-naphthaleneazothymol by Baumann's reaction. It is best purified by crystallizing first from benzene-ligroin and finally from alcohol. Melting-point 173°.5. The melting-point is not raised above 170° by crystallization from benzene-ligroin alone.

0.1823 gram substance gave 0.5312 gram CO_2; and 0.1026 gram H_2O.

0.2500 gram substance gave 16.3 cc. N at 28° and 743 mm.

	Calculated for $C_{27}H_{24}N_2O_2$.	Found.
C	79.41	79.47
H	5.88	6.25
N	6.86	7.066

The compound is readily soluble in ether and benzene, less so in ligroin, and with difficulty in alcohol. From benzene and alcohol it crystallizes in needles. On saponification it yields α-naphthaleneazothymol.

CHEMICAL LABORATORY,
OHIO STATE UNIVERSITY.

ACTION OF PHENOLS ON ETHYLIC OXALATE.

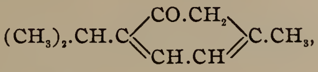
BY J. BISHOP TINGLE AND LEO O'BYRNE.

Theoretical.

In the course of a paper on camphoroxalic acid derivatives by one of the present writers and Alfred Tingle,[1] a description was given of an experiment on the interaction of ethylic oxalate and thymol, in the presence of sodium. The product was obtained in the form of an oil, and gave a dark-red coloration with alcohol and ferric chloride. The most obvious explanation of the condensation is that the thymol had reacted in its secondary form

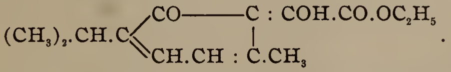
---

[1] This JOURNAL, **21**, 261 (1899).



$$(CH_3)_2.CH.C\begin{array}{l} \diagup CO.CH_2 \diagdown \\ \diagdown CH.CH \diagup \end{array} C.CH_3,$$

producing the compound



$$(CH_3)_2.CH.C\begin{array}{l} \diagup CO\text{———}C : COH.CO.OC_2H_5 \\ \qquad\qquad\qquad\;\, | \\ \diagdown CH.CH : C.CH_3 \end{array} .$$

We thought that it might be interesting to examine the matter more closely, and we have accordingly tested the behavior, under similar circumstances, of a number of phenols and allied compounds. The results given in the present paper are only to be regarded as preliminary, but, as the work will suffer interruption for a time, it appears desirable to place our observations on record. In addition to thymol the following compounds were investigated: pyrocatechol, carvacrol, picric acid, β-naphthol, ethylic salicylate, quinone, guaiacol, resorcinol, phloroglucinol, hydroquinol, anisoïl, and carvol. Of these the first six showed no sign of having reacted. Guaiacol yielded tarry products which could not be investigated. Anisoïl and carvol, as was to be anticipated from their constitution, yielded condensation-products of the desired kind. Resorcinol, phloroglucinol, and hydroquinol also yielded compounds. That from the first melted and decomposed at 257°–258°, and is possibly identical with the substance which Michael[1] obtained by the interaction of resorcinol, ethylic oxalate, and dry sodium ethoxide at 200°. It gives a red coloration with ferric chloride and alcohol. The compound from phloroglucinol also gives a reddish color with ferric chloride and alcohol. It is incompletely melted at 305°, and may possibly prove to be an oxidation-product of the phenol. Hydroquinol yielded a substance which was somewhat difficult to purify. It blackened above 200°, was not melted at 300°, and gave no coloration with alcohol and ferric chloride. It is very probable that this compound also is formed as the result of oxidation.

---

[1] J. prakt. Chem., [2], 35, 510.

Experimental.

In all cases, unless otherwise stated, the experiments were performed in the following manner: ethylic oxalate and the phenol, or other compound, were mixed in equidecigram molecular proportion, light petroleum (300 cc.), which had been thoroughly dried, was added, then an atomic proportion of sodium wire. The flask containing the mixture was connected to a reflux condenser, and, if needful, heated on the water-bath. After the sodium had dissolved, the flask, suitably protected from moisture, was allowed to remain at the ordinary temperature during about twenty hours; the contents were then poured into water, the light petroleum removed, and the aqueous liquid extracted two or three times with ether; this was removed, an excess of dilute sulphuric acid added to the aqueous solution, and the extraction with ether repeated several times. The light petroleum and ether extracts were dried by means of calcium chloride, and distilled from the water-bath. For the sake of brevity, the combined ethereal extracts, before acidification of the aqueous liquid, will be termed in the following pages "ethereal extract 1," while the combination of those made after the addition of acid will be referred to as "ethereal extract 2."

Pyrocatechol.—On account of the sparing solubility of this compound in light petroleum, absolute alcohol was employed in its place. The sodium was first dissolved in the alcohol, then the other two ingredients added. The subsequent procedure was exactly that described above. From neither of the ethereal extracts was anything but pyrocatechol recovered.

Carvacrol.—The experiment was carried out in the usual manner. The light petroleum extract consisted of an oil which proved to be carvacrol. The ethereal extract 2 showed signs of crystallization (oxalic acid?) but contained carvacrol; as it is probable that any condensation-compound (ethylic salt) would crystallize with much greater difficulty than the free acid, corresponding with camphoroxalic acid, the substance was hydrolyzed and the product purified, but no new compound could be detected.

Picric Acid.—This experiment was carried out in exactly the same manner as that with pyrocatechol, and gave a similarly negative result.

β-Naphthol.—This substance behaved like carvacrol in all respects. The ethereal extract 2 was tarry, melted at about 160°, and was not further investigated.

Ethylic Salicylate.—The modification of E. Fischer's method, which has been previously described by one of us and Alfred Tingle,[1] was advantageously employed for the preparation of this compound. Salicylic acid (50 grams) was mixed with 95 per cent alcohol (300 cc.) and concentrated sulphuric acid (15 cc.), and boiled in a reflux apparatus during seven hours. The greater portion of the alcohol was removed on the water-bath, the residue neutralized with sodium hydrogen carbonate, dissolved in water, and extracted with ether. The yield is excellent, but is improved by the use of a pressure bottle.[2] With this appliance, salicylic acid (40 grams), 95 per cent alcohol (150 cc.), and concentrated sulphuric acid (24 cc.), after being heated at 100° during four hours, yielded 40 grams of ethylic salicylate and 5.9 grams unchanged acid. In another experiment the alcohol and sulphuric acid were reduced to 100 cc. and 16 cc. respectively, without any special effect on the yield, the other conditions remaining unchanged; the chief factor of importance is apparently to keep the proportion of sulphuric acid somewhat high. No new compound could be isolated by treating ethylic salicylate with ethylic oxalate and sodium in the ordinary manner, a result fully in accordance with expectation.

Quinone.—In order to dissolve the sodium in this case, it was necessary to add about 200 cc. absolute alcohol to the light petroleum; the mixture immediately turned black. The subsequent working of the product was attended with difficulty on account of the formation of emulsions. The result was similar when sodium ethoxide, dissolved in absolute alcohol, was substituted for the sodium and light petroleum.

Guaiacol.—Gave entirely negative results.

---

[1] This Journal, 21, 255 (1899).

[2] We are indebted for these details to Dr. A. Tingle, of Columbia University, New York.

Resorcinol.—In order to obtain a solution of the sodium it was necessary to add absolute alcohol (150 cc.) to the solution of the materials in light petroleum. The ethereal extract 1 deposited resorcinol, melting at 110° to 111°. The ethereal extract 2 yielded yellow crystals which, after purification by means of alcohol, melted and decomposed at 257°–258°. The compound darkens below its melting-point, is very readily soluble in alcohol, and the solution gives a red coloration with ferric chloride. It is hoped that light may be thrown on the nature of this compound by its subsequent investigation.

Phloroglucinol.—As in the case of resorcinol, it was necessary to add absolute alcohol in order to cause solution of the sodium. The ethereal extract 1 deposited a compound which crystallized from alcohol in colorless plates and remained unmelted at 240°; somewhat below this temperature it blackened. No coloration was produced with alcohol and ferric chloride. Ethereal extract 2 also deposited crystals which were purified like the others. They softened, but did not melt, at 305° and gave a reddish coloration with alcohol and ferric chloride.

Hydroquinol.—The sodium remained practically unattacked after heating for some time, a little benzene was therefore added, but this only caused the formation of a brown crust on the metal. Then absolute alcohol (100 cc.) was poured in, whereupon the mixture immediately blackened. The ethereal extract 1 apparently only contained unchanged phenol. The ethereal extract 2 did not change with alcohol and ferric chloride. It was digested with sodium hydroxide, acidified, and digested with sodium carbonate solution to separate any acid from phenol; as the solution was quite clear it was acidified, and the black precipitate removed and dried. Extraction of it by means of alcohol and benzene left a tarry mass, which was not further investigated, and a white solid; this blackened above 200°, but remained unmelted at 300°.

Anisoïl.—This also required the addition of absolute alcohol (100 cc.) to dissolve the sodium. The light petroleum gave no residue. The ethereal extract 1 yielded an oil which gave no color with ferric chloride and alcohol. The ethereal extract 2 was oily but gave a deep-red coloration with ferric chloride and alcohol, showing that the desired condensation had taken place.

Carvol.—This reacts readily in light petroleum solution. The product was obtained from both the ethereal extracts as well as from the light petroleum. The new compound gives a deep-red coloration with ferric chloride and alcohol and is oily. After hydrolysis an oil was also obtained which forms a barium and copper salt, but they are difficult to purify and, like the parent substance, readily become resinous. The resin has a strong odor of violets.

The work will be continued and extended in various directions.

LEWIS INSTITUTE, CHICAGO, ILL.

Contribution from the North Carolina Experiment Station.

THE DETERMINATION OF PENTOSANS.

BY G. S. FRAPS.

The term "pentosan" is applied to those substances occurring in vegetable materials which yield furfural when distilled with hydrochloric acid, though their nature is a problem as yet unsolved. The method of determining pentosans consists in distilling the substance with hydrochloric acid of 1.06 sp. gr., and precipitating the furfural in the distillate with phloroglucol. It is assumed that the only product in the distillate which is precipitated by phloroglucol is furfural, but this is not the case. As already pointed out by the writer,[1] small quantities of insoluble fatty acids pass over into the distillate, which, while not precipitated by furfural, appear in the distillate unless previously filtered out. Further, if the distillate is allowed to stand ten or more hours, very often an amorphous black precipitate separates, which would also appear in the distillate, either as such or combined with the phloroglucol, since the vessel is always allowed to stand over night after adding the precipitating agent. Finally, the distillate always contains one or more substances which do not appear to be furfural, and which are precipitated by phloroglucol. These substances will be discussed in the following pages.

---

[1] Bull. 172, 56, North Carolina Experiment Station.

Furaloid.

While carrying through the determination of pentosans in a number of materials, the possibility that the distillation with hydrochloric acid might destroy some of the furfural occurred to the writer. This possibility seemed stronger than when one of the distillates was evaporated and found to leave a brown residue. To test the point further, corn bran was distilled with hydrochloric acid in the usual way for the determination of pentosans, and the distillate divided into two equal portions. One portion was made up to 500 cc. with acid, and precipitated with phloroglucol. The second portion (200 cc.) was placed in a distilling flask and 170 cc. distilled. The distillate was returned to the flask, distilled to a small volume, 30 cc. acid added, distilled, and the addition of acid and distillation repeated once more. The distillate was made up once to 500 cc., and the furfural precipitated with phloroglucol. The weights of the precipitates were, from :

	Gram.
Undistilled portion	0.2216
Distilled portion	0.1715
Loss	0.0501
Loss, per cent	22.5

Other experiments gave the same result, though the loss was not so great, as the second distillation was never carried out twice.

The question arose, is this loss due to oxidation during the second distillation ? That it was not is shown by the fact that the loss was as great when the distillation took place in a current of carbon dioxide as in the air. In performing this experiment, the distillate was divided into several portions, and two portions precipitated directly, after dilution to 500 cc. with hydrochloric acid of 1.06 sp. gr. The other portions were placed in distilling flasks and distilled almost completely, then 30 cc. of acid were added, and distilled. The addition of acid and distillation was repeated several times, the distillate then made up to 500 cc., and precipitated as before. This is the method used in all subsequent experiments, unless otherwise noted.

Timothy hay was the material used. The weights of the precipitates were, from :

	I. Gram.	II. Gram.
Undistilled portions	0.2763	0.2767
Distilled alone	0.2299	....
Loss, per cent	16.8	....
	Gram.	Gram.
Distilled with CO_2	0.2216	0.2236
Loss, per cent	19.1	19.8

The loss was not caused by oxidation during the second distillation.

Is this loss due to decomposition of furfural? was the next question. To test this point, freshly prepared furfural was dissolved in hydrochloric acid of 1.06 sp. gr., and portions distilled as in the preceding experiment. The precipitates weighed, from :

	Gram.	Gram.
Undistilled portions	0.2815	0.2805
Distilled portions	0.2804	....
Loss	none	....

After standing four days the solution of furfural became brown, probably by oxidation. In this condition it gave the following results :

	Gram.	Gram.	Gram.
Undistilled portions	0.2880	0.2863	.....
Distilled portions	0.2785	0.2779	0.2762
Mean loss			0.0096
Loss, per cent			3.2

The error of analysis may be 0.0030 on each precipitate, so that the loss is very small.

The possibility still remained that during the first distillation of the substance with hydrochloric acid the furfural formed is changed, by oxidation or otherwise, so that it does not pass over during the second distillation. To test this possibility, a solution of the furfural was prepared and distilled in the usual way. One portion of the distillate was distilled as before, and a second portion precipitated directly. The results follow:

	Gram.
Distilled once	0.4577
Distilled twice	0.4510
Loss	0.0065
Loss, per cent	1.5

The loss is less than when the furfural solution had stood four days.

These experiments seem to show that when vegetable materials are distilled with hydrochloric acid there may be formed, besides furfural, a substance or substances which precipitates phloroglucol, and is destroyed (in part or wholly) by a second distillation. Until more is learned as to the nature of this substance, for convenience's sake, I shall use the term furaloid to designate it.

Occurrence of Furaloid-yielding Substances.

The furaloid-yielding substances were determined in the manner already noted, namely, the material was distilled with hydrochloric acid, the distillate divided into two portions, and one portion distilled again. The percentage lost was assumed to represent the percentage of furaloids present in the crude furfural. This method is not supposed to be very accurate, but only to give some idea as to the occurrence of these substances.

The furaloid-yielding substances are widely distributed in nature as all the materials tested contained them. The table shows the percentage obtained by the method just described.

Furaloid in Crude Furfural.

	Weight lost. Gram.	Per cent lost (furaloid).
Cottonseed meal	0.0301	7.4
Cowpea meal	0.0197	17.9
Crimson clover hay	0.0337	11.7
Irish potato vines	0.0278	10.2
Corn bran	0.0501	22.6
Timothy hay	0.0596	18.1
Pine straw	0.0241	13.2
Gum arabic	0.0338	12.9
Corn cobs	0.0595	10.1
Okra hulls	0.0513	11.5
Oak sawdust	0.0311	6.9
Oxycellulose	0.0148	13.8

None of these losses are small enough to be ascribed entirely to change in furfural. In the table the distillates from the materials down to pine straw were allowed to stand over night and filtered before being distilled. The distillates from pine straw and the others were redistilled the same day as prepared. The oxycellulose was prepared by oxidizing filter-paper with chromic acid in the presence of sulphuric acid.

In some cases the residue in the flask was evaporated to dryness in a platinum dish, dried, weighed, ignited, and weighed again. The organic matter so determined was, as a rule, about 50 per cent of the loss in weight of the phloroglucid precipitate, but it varied considerably. On account of this variation, as it is not certain that the furaloid was changed to non-volatile substances, little value was attached to these figures, and they are not given.

Distribution of Furaloid-yielding Substances.

When substances containing pentosans are boiled with 1.25 per cent sulphuric acid, and then with 1.25 per cent caustic soda, as for the determination of crude fiber, part of the pentosans is dissolved by the acid, part by the alkali, and usually a part remains in the crude fiber.

In order to ascertain to what extent the furaloid-yielding bodies were dissolved by 1.25 per cent sulphuric acid, 10 grams of the material were boiled for half an hour with a liter of the acid, filtered, and washed. The residue was distilled with hydrochloric acid and furaloid determined in the distillate. The filtrate was neutralized with barium carbonate, filtered, evaporated to a small volume, and distilled with hydrochloric acid. Furaloid was determined in the distillate. Furfural was given off during the evaporation.

Furaloid in Crude Furfural.

	Entire material. Per cent.	Dissolved by acid. Per cent.	Undissolved. Per cent.
Corn bran	22.6	0.0	6
Timothy hay	18.1	7.3	2
Crimson clover hay	11.7	7.0	1

The furfuraloid-yielding substances were almost completely dissolved by the acid and at the same time destroyed entirely, or to a great extent.

About 90 per cent of the pentosans in the corn bran and 45 per cent of those in the timothy hay were dissolved by the acid.

Digestibility of the Furaloid-yielding Substances.

One experiment was made to see if the furaloid-yielding bodies were more or less digested than the pentosans. The furaloids were determined in the distillate from the excrement from a sheep fed timothy hay, which had been used in digestion experiments.

	Per cent.
Pentosans digested in hay	55.9
Furaloids in crude furfural from hay	18.1
" " furfural from excrement	10.7

The furaloid-yielding bodies have disappeared to a greater extent than the pentosans and must be digested. From the above figures their digestibility is about 75 per cent compared with 60 per cent for that of the pentosans.

Determination of Pentosans.

It appeared possible that the substances here called furaloids were formed from the true pentosans (anhydrides of pentose sugars) by distillation with hydrochloric acid, and their presence did not affect the pentosan determination. The contrary seems to be true. To test this point, a pentose sugar was prepared and tested in the following way: Finely-ground corn cobs were extracted with dilute ammonia and hydrolyzed with dilute hydrochloric acid. The acid was neutralized with lead carbonate, the liquid evaporated to a small volume, two volumes of alcohol added and filtered. The filtrate was evaporated to a small volume, and xylose No. 1 precipitated with absolute alcohol. The alcohol was partly evaporated, water added, and the solution saturated in the cold with barium hydroxide. The impure barium compound of the sugars was precipitated by adding alcohol (xylose No. 2). Both of these materials were impure, but sufficiently pure for the end in view.

They were distilled with hydrochloric acid and furaloid determined in the crude furfural of the distillate. The weights of the precipitates were:

	Xylose No. 1.		Xylose No. 2.	
	Gram.	Gram.	Gram.	Gram.
Undistilled	0.1555	0.1594	0.0257	0.0250
Distilled	0.1524	0.1530	0.0257	0.0240
Loss, per cent	2	4	0	0

With these figures may be compared those obtained from the products of the hydrolysis of corn bran, timothy hay, and crimson clover hay. In detail these were:

	Bran. Gram.	Timothy hay. Gram.	Crimson clover hay. Gram.
Undistilled	0.5025	0.2891	0.0829
Distilled	0.5025	0.2680	0.0772
Loss	0.0000	0.0110	0.0057
Loss, per cent	0	7.3	7.0

Allowing for error of analysis the differences are small. It seems probable that furaloids are not formed by distilling pentose sugars with hydrochloric acid. Accepting this as true, it is evident that the presence of furaloids in the crude furfural affects the determination of the pentoses. Until we know more about the pentosans, and the furaloid-yielding substances, it is questionable whether it would be expedient to determine them separately, since they can very conveniently be grouped together. A method of separating the furaloid from the crude furfural was tested, as follows: The vegetable material was heated two hours under a reflux condenser with hydrochloric acid, instead of distilling off directly. The condenser was then turned down and the furfural distilled as usual. A brown substance was deposited in the tube of the condenser. Furaloids were determined in the distillate and found to be: Timothy hay, 1 per cent; okra hulls, 5 per cent; excrement, 3 per cent; corn silage, 14 per cent. The furaloids were destroyed, except in the case of the silage. It is feared that this method would give too low results for furfural.

Summary.

The distillate from vegetable materials with hydrochloric acid may contain, besides other things, fatty acids, a substance which separates as a black precipitate if the vessel is allowed to stand, and a substance or substances which is destroyed by distilling again (furaloid). All three of these may appear in the phloroglucol precipitate.

The furaloid-yielding bodies were found in all the materials tested, the crude furfural in the hydrochloric acid distillate containing from 7 to 23 per cent furaloid.

The furaloid-yielding bodies are hydrolyzed by boiling 1.25 per cent sulphuric acid, and lost in the subsequent evaporation. They are digested to a greater extent than the total pentosans in the one sample of timothy hay excrement tested.

The furaloid is not formed by the action of the hydrochloric acid on pentose sugars.

The work above described was done in the laboratory of the North Carolina Experiment Station, with the permission of Prof. W. A. Withers, chemist.

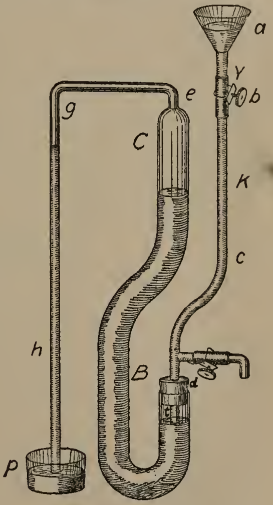
AN EASILY CONSTRUCTED BAROMETER.

By George W. Russell.

The necessity of a barometer in every chemical and physical laboratory, and the refusal of a prominent dealer to guarantee the safe arrival of the convenient Bunsen, or siphon, form make desirable some simple and efficient means of filling this piece of apparatus, and the following device has been found to work well. As is well known, the boiling of a large quantity of mercury in straight glass tubes, except under diminished pressure, is troublesome and dangerous, and in the siphon tubes it is almost impossible.

By the method here described, so diminished a pressure over the top of the column of mercury can be maintained that all air and water vapor, except the smallest trace, can be gotten rid of, and a barometer obtained sufficient for all but the most exacting gas analyses, and any one who can seal two glass tubes together can make it. The cost is trifling. The error in measuring the height of the siphon barometer is ordinarily 0.1 mm., and this is much greater than the depression due to the vapor remaining in a tube filled as described in this note.

A tube B C of suitable diameter (say 8 to 10 mm.) and with walls of medium thickness is drawn out at *e* to a suitable capillary, and then bent into the siphon form. It is then covered with wax and graduated according to the well-known method of Bunsen, and etched with liquid hydrofluoric acid (the acid may be conveniently applied with a tuft of cotton fastened to the end of a platinum wire), cleaned with a hot solution of sulphuric acid and potassium bichromate, washed with distilled water, and thoroughly dried.



Now seal to BC, at *e*, a tube, *gh*, of about 0.6 mm. internal diameter and bent as shown, with *gh* about 800 mm. long. The tube *kct* is about 1 mm. internal diameter, bent as shown, and fitted into B C by a good cork. The apparatus is clamped in position and a train of U-tubes containing sulphuric acid is attached to *kct* at the rubber connection *y*, and air aspirated through the system till all water vapor is removed, then the funnel *a* is attached and a small cup *h* containing mercury placed under the end of the tube *gh*. Mercury at a temperature of 105° to 120° is slowly filtered through the tube *kct* until the bend is filled 40 to 50 mm.; then close clamp *b* and open clamp *d* so that the mercury in the bend may rise above the end of *t*. Now close clamp *d*, open *b*, and slowly filter the hot mercury into the barometer tube, meanwhile carefully running a Bunsen flame up and down B C. After the tube is filled and the mercury runs over into *p*, open the clamp *d*, and allow the mercury to flow out at clamp *d* and fall in B C. The mercury can now be heated to boiling and kept at this temperature for some time, then close *d* and filter more mercury into B C till it fills the capillary and runs over into *p*. This process can be repeated indefinitely, but one repetition is usually sufficient. Before sealing off *e* it is best to allow the system to stand a day or so. Seal off the capillary at *e*, take out the cork and filling tube, and set up the barometer in the usual position.

In this way can be made, in the laboratory, an inexpensive barometer, and one sufficiently accurate for all ordinary experimental work of the student. The tubes can be bent and graduated as indicated or they can be purchased ready for drawing out and sealing to the capillary.

HIGH SCHOOL, ROANOKE, VA.,
March 13, 1901.

OBITUARY.

FRANÇOIS MARIE RAOULT.

With the death of Raoult in Grenoble, on April 1st, 1901, France has lost her most prominent physical chemist. The importance of the work of Raoult on the development of modern physical chemistry is not easily overestimated. He was the first to point out clearly, as the result of elaborate experimental investigations, the laws of the lowering of the vapor-tension and of the freezing-point of solvents by dissolved substances. He found that those substances which, in solution, conduct the current and are, therefore, known as electrolytes, give greater lowering of vapor-tension and of freezing-point than the non-electrolytes. We all know the importance of this discovery. It was to account for these facts, together with the greater osmotic pressure exerted by the electrolytes, that Arrhenius proposed the theory of electrolytic dissociation. The work of Raoult on lowering of freezing-point and lowering of vapor-tension, together with that of Pfeffer on osmotic pressure, form the foundation of the new physical chemistry.

Raoult's work is by no means limited to the study of the lowering of the freezing-point and of the vapor-tension of solvents. It should, however, be stated that probaby the most accurate cryoscopic measurements which have ever been made are those which were recently published by Raoult. His earlier work had to do with problems of a purely physical nature. Indeed, one of his earliest investigations threw much light on the action of the voltaic cell.

In thinking of Raoult we must not confine ourselves to the work which he has done, as brilliant as it is, but must remember the noble character and unassuming manner which were his characteristics. Abundant testimony to these attributes is furnished by all who knew Raoult, and the kind heart and singleness of purpose of his life are obvious to any one who has been favored with a line from his pen.

Raoult was born May 10, 1830, at Fournes (Nord), and was, therefore, nearly seventy-one years old when he died. The last thirty years of his life were spent at Grenoble in scientific investigation and in building up the institution with which he was connected. In 1889 he was elected dean of the faculty of sciences, a position which he held until his death.

He was loved by all who knew him and admired by all true men of science. H. C. J.

REPORTS.

The Action of Water upon Rocks.[1]

A recent number of this JOURNAL[2] contained a review of the work of Gautier upon the combustible gases present in the atmosphere and the probable source of the hydrogen existing there in a free condition. The results obtained led to an investigation of the probable origin of the gases which escape from the earth and their formation from the rocks. Reports of these researches show that the formation of the gases and the composition of many complex rocks can be explained readily without the assumption of any exterior agent. The escape of gases in mineral waters and from volcanoes and the cause, perhaps, of the violence of volcanic eruptions are explained and demonstrated by experiment. The author remarks that it may appear rather paradoxical to expect to obtain any results by heating rocks which were originally formed from a fused mass and have been exposed to the action of heat for centuries, the intensity of the heat depending upon the depth of the rocks below the surface. A fact of great importance, and one which must be taken into consideration, is that the rocks were subjected to a pressure sufficient to prevent dissociation. If, however, conditions of pressure were changed, the possibility of reactions arose, and it was this problem which attracted the attention of the investigator.

---

[1] Gautier: Compt. rend., **132**, 58, 189, 518, 740, 932.

[2] This JOURNAL, **25**, 344.

When granite is heated to 100° with acid or to 300° with water alone a large volume of gas is formed. In two experiments, in each of which 1000 grams of granite, quarried from the same place at intervals of eight months, were heated in a vacuum to 100° with phosphoric acid and water, the following amounts of gas, calculated at 0° and 760 mm. pressure, were obtained :

	Volume of gas in cc.	
	I.	II.
HCl, $SiFl_4$	trace	trace
H_2S	1.33	22.7
CO_2	272.6	237.5
Hydrocarbon absorbed by bromine	12.3	5.3
CH_4	trace	trace
H	53.05	191.48
N and argon	232.50	102.48
	571.78	559.46

Specimens heated with water alone to 300° gave the following results :

H_2S	1.3	1.0
CO_2	7.2	5.3
H	46.00	14.6
N	0.3	5.9

Soluble sulphides, which did not previously exist in the water, were found after the action was over and a comparison of the gas with that from volcanoes showed a strong resemblance.

The author shows that, in order to explain the action taking place in the earth, it is not necessary to assume, as is generally done, that surface water should penetrate to the seat of the action, as the rocks contain sufficient water to cause a very considerable decomposition. That this water is not present as water of constitution is shown from the fact that the rate and amount given off is not regular, but dependent upon the temperature. The results obtained with four varieties of rocks, representing both acid and basic varieties, show that all varieties of rocks contain large amounts of water:

	Loss per 1000 grams of rock.	
	15°–250°.	250°–1000°.
Granite	2.29	7.35
Porphyry	5.80	12.40
Ophite	....	15.06
Lherzolite	....	16.80

The following results will give some idea of the amount of gas that can be formed and its relation to the volume of the rock:

Granite. Acid rock.	I.	II.	III.
Total vol. at 0° and 760 mm. pressure per 1000 grams of rock	2709 cc.	4209 cc.	2570 cc.
Composition per 100 volumes:			
CO_2	14.80	8.98	14.42
H_2S	trace	1.71	0.69
CO	4.93	5.12	5.50
CH_4	2.24	1.09	1.99
H	77.30	82.80	76.80
N and Ar	0.83	0.42	0.40
	100.10	100.12	99.80
Volume calculated for 1000 grams of rock:			
CO_2	400.6	378.0	370.6
H_2S	trace	71.9	18.7
CO	133.4	215.2	141.3
CH_4	60.6	45.8	51.1
H	2092.5	3481.0	1977.7
N	22.7	10.6	10.3
	2709.5	4209.5	2569.7

1000 grams or 376 cc. of granite, gave an average of 3162 cc. of gas, or 6.7 times its own volume. In a similar way another acid rock, porphyry, gave about 7.6 times the volume of the rock. Ophite, a basic rock, gave 7.6 times the volume of the rock, while lherzolite gave 15.7.

We see, therefore, that from 100 vols. of granite 670 vols. of gas were obtained; from 100 vols. of porphyry 760 vols. of gas were obtained; from 100 vols of ophite 760 vols. of gas were obtained ; while from 100 vols. of lherzolite 1570 vols. of gas were obtained.

The assumption that the gas is present as such in the rocks is no longer tenable, as some of these rocks have no cavities and the gas would have to be under a pressure sufficient to liquefy carbon dioxide.

If the gases were present as such in the rock they should be evolved at a constant rate when the rock is heated, but the following experiments show that this is not the case :

Granite.	First third.	Balance.
CO_2	20.19	6.13
H_2S	1.28	0.41
CO	0.57	1.02
CH_4	2.04	0.80
H	75.54	91.64
N	0.30	0.30
	99.92	100.30

A somewhat similar result was obtained when ophite was used.

As the action in the interior of the earth is causing constant weakening in some places and upheavals in others, there is abundant opportunity for fresh portions of rock to come under the influence of a greatly increased temperature and undergo changes similar to those which occur in the laboratory under similar conditions. There is no need to call to our aid any mysterious agent in order to explain volcanic explosions, as we find that the amount of gas formed, by the action of the enclosed water on the rock, is sufficient to explain the great explosive power. We can get a better idea of this, perhaps, when we consider that 1000 cc. of granite give, at 1000°, 20 liters of gas and 89 liters of water vapor.

As has already been pointed out, the hydrogen does not exist as such in the rock, but is formed by the action of the water on the rock. If many ferrous salts are heated to 750° or 800° with steam, hydrogen and an oxide of iron are formed, while ferrous sulphide yields a mixture of hydrogen and hydrogen sulphide, the proportion of the latter diminishing as the temperature increases. If siderite, the natural carbonate of iron, is heated with water, the following gases are formed : carbon dioxide, carbon monoxide, hydrogen sulphide, hydrogen and nitrogen. The nitrogen is formed from the nitride present as an impurity and the carbon monoxide is formed by the reduction of the carbon dioxide by the oxide of iron. As a similar reaction takes place when a silicate of iron is heated with steam we can understand how mica, hornblende, pyroxene, biotite, etc., form hydrogen when they are heated with steam. If the hydrogen is confined and under pressure the reverse action takes place with the formation of ferrous salts, and this interchange continues until a state of equilibrium is reached when both ferrous and ferric silicates, such as are commonly found in the micas, pyroxenes, etc., are present. In an experiment carried out in the laboratory, 150 grams of ophite were heated to 250° to expel water and then to red heat, when 2.25 grams of water of constitution and 371 cc. of gas were formed. This residue was then cooled in a vacuum and heated with steam, when 70 cc. of gas were obtained. This gas could not have preexisted in it, but was formed by the action of the water.

The fact that, besides the gases already mentioned, hydrogen sulphide, marsh gas, and others are found in small quantity in the gases escaping from the earth requires explanation, and this subject has received attention. As already stated, the hydrogen is due to the decomposition of the iron compounds and silicates by water vapor, the carbon dioxide to dissociation of the carbonates and the carbon monoxide partly to reduction of carbon dioxide.

The author has devised a method for detecting free hydrogen sulphide, soluble sulphides, polysulphides, and hyposulphites in the same solution, and tests made with natural and artificial waters have led to the same conclusion as that reached by Henry, Boullay, and others, that the majority of sulphur waters contain the sulphur as an alkaline sulphide (nearly always sodium sulphide) with small amounts of sulphydrate, the proportion of the latter depending upon the amount of carbon dioxide present. The method used in this separation consists in distilling the water in a vacuum when the free hydrogen sulphide is driven out. If now carbon dioxide is passed through the solution, in which the temperature is kept below 30°, the soluble sulphide is decomposed with the formation of hydrogen sulphide, which is expelled as before. The sulphur in the form of hyposulphites is determined by titration with an iodine solution, and the sulphur of the polysulphides, after being liberated by acid, is oxidized by nitric acid and determined as barium sulphate.

Owing to the fact that sulphur waters escape from the earth from deposits that contain no soluble sulphur compounds, it has been difficult to explain their origin. The results obtained in this work, however, show that the formation can be readily explained on the basis of laboratory experiments. If powdered granite is treated for some time with cold water and the solution tested, it is found to be free from hydrogen sulphide and alkaline sulphides and contains chiefly silicate of soda and calcium sulphate. This test, as carried out, shows that no sulphides of the alkalies or alkaline earths are present in the granite. If, however, the granite is heated, in a sealed tube, with water to 250° to 300°, a true artificial sulphur water is formed which has the characteristic odor and alkaline reaction, and in which sodium sulphide, ammonium salts, phosphates, sulphates, and silicates, carbon dioxide, and nitrogen can be detected. As the test with cold water shows the absence of soluble sulphides and as the sulphide of iron does not react with water except at a high temperature and other metals, whose sulphides are decomposed by water, are not present, the formation of hydrogen sulphide cannot be ascribed to these substances. When an igneous rock is heated to redness, several gases, including hydrogen and carbon monoxide, are formed.

If now these gases are retained in cavities in the rocks and subjected to high pressure, they, along with carbon, in the presence of hydrogen sulphide, formed by the action of water on the sulphide of iron, act upon the feldspars, kaolins, etc., to form sulphosilicates and oxysulphides. These substances would be decomposed by hot water; but, under the action of pressure as the mass cooled, a condition of equilibrium would be reached when small amounts of the sulphur compounds would remain in the rocks. These substances, when heated with water, form soluble sulphides and hydrogen sulphide, and it is to these, present in small quantities in the rock, that the sulphur gases of mineral waters owe their origin.

If some albite is heated with water to 300° there is no trace of hydrogen sulphide formed; but if the material is placed in a tube, which also contains some granite, so arranged that the gases formed from the granite can react, under pressure, upon the albite, the latter, after this action, yields, when heated with water, hydrogen sulphide. This action is due to the formation of sulpho and oxysulpho compounds, some of which have been isolated in pure crystalline condition.

The ammonium salts which are so often found in mineral waters are formed, along with the nitrogen, by the action of water on the nitrides, which have been detected in the igneous rocks and in several cases isolated in a crystalline condition. Iodine and arsenic, which also commonly accompany sulphur compounds in mineral waters, have been detected by Gautier in the rocks from which the waters are charged with their solid and gaseous constituents.

We can thus explain the origin of all the gases occurring in volcanic gases and in mineral waters by the action of water and heat on substances present in the igneous rocks, the hydrogen sulphide being formed by the action of water on the sulphosilicates and oxysulphide of carbon, the carbon dioxide by dissociation of carbonates, the carbon monoxide by reduction of the carbon dioxide, hydrogen by the action of water on ferrous silicates, hydrocarbons from the carbides, nitrogen and ammonium salts from the nitrides, and the sulphocyanates from the action of the ammonium salts and carbon dioxide.

These results, based on laboratory experiments, offer, therefore, a simple explanation of reactions which have hitherto been considered inexplicable. J. ELLIOTT GILPIN.

REVIEWS.

ENGINEERING CHEMISTRY: A Manual of Quantitative Chemical Analysis, for the Use of Students, Chemists, and Engineers. By THOMAS B. STILLMAN, M.SC., PH.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. Second edition. Easton, Pa.: The Chemical Publishing Co. 1900. pp. xxii + 503.

This second edition of Professor Stillman's book does not very greatly differ from the first, published in 1897. The number of pages is a little smaller, and there are not quite so many illustrations. The omission of a few subjects which had no proper place in a work on chemistry as applied to engineering is an improvement, a few useful additions have been made, and some changes in the order in which the various subject-matters are taken up have also been advantageous. But nothing has been introduced in regard to lime, lime mortar, stucco, or explosives, although these should certainly receive notice in a work on engineering chemistry. And, almost without exception, individual errors pointed out in a notice of the first edition remain uncorrected. J. W. M.

ANORGANISCHE FERMENTE. Darstellung kolloidaler Metalle auf elektrischem Wege, und Untersuchung ihrer katalytischen Eigenschaften. Kontaktchemische Studie von DR. PHIL. GEORG BREDIG, Privatdozent der Chemie a. d. Universität Leipzig. Mit 6 Figuren im Text. pp 99. Leipzig: Wilhelm Engelmann. 1901.

This monograph is an outgrowth of the important paper by Bredig and von Berneck on "Inorganic Ferments," which appeared in the Jubilee volume of the Zeitschrift für Physikalische Chemie, which was dedicated to van 't Hoff by his students. The original paper has been largely supplemented by an introductory chapter on methods of preparing colloidal solutions of the metals, and by subsequent experimental work with Ikeda and Reinders.

The general method employed in preparing colloidal solutions of the metals consists in passing a suitable current between two bars of the metal immersed in pure water. In this way solutions of platinum, iridium, gold, palladium, silver, cadmium, etc., have been obtained.

The second part of the monograph deals with the properties of such solutions, and especially with their catalytic decomposition of hydrogen dioxide. The author sees in the contact action of these colloidal solutions of the metals an analogy to the action of organic ferments, whence the title of the monograph. A very small amount of platinum in solution in water can decompose a large amount of hydrogen dioxide. This action can be prevented by the presence of mere traces of certain substances like hydrogen sulphide, hydrocyanic acid, etc., a fact that suggests the action of very small quantities of certain poisons on organic ferments.

The work is extremely interesting, not only to the physical chemist but to the physiologist, and can be heartily recommended to all who have to deal in any way with the subject of fermentation. H. C. J.

CORRESPONDENCE.

Moscow, the 2/15 April, 1901.

To the Editor:

Sir: I beg you to accept my most sincere thanks for your friendly congratulations on the occasion of the celebration of my fortieth year of service.

Finding it quite impossible to address my heartfelt thanks directly to every one of all the American chemists who did me the honor to send me their congratulations, I beg that you will have the kindness to let me express to them the sentiments of my deepest gratitude in the pages of the American Chemical Journal, by inserting there this letter.

Accept, sir, the expression of the most distinguished salutation of

Yours very truly,
Prof. Dr. H. Markownikoff.

CORRECTIONS.

✓ Vol. 24, page 257, line 9: *After* "silver" *insert* "per cubic centimeter."

✓ Vol. 24, page 258: The last equation should be

$$\overset{-}{NO_3} + \overset{-}{NO_2} + 2\overset{++}{Ag} + I_2 + H_2O = 2AgI + 2\overset{++}{H} + 2\overset{--}{NO_3}.$$

✓ Vol. 24, page 259, line 8: *For* "Danner" *read* "Dorrer."

INDEX VOL. XXV.

AUTHORS.

ALLAN, F. B. The basic nitrates of bismuth 307
Allen, A. H. Commercial organic analysis (Review) 88

BLAIR, A. A. The chemical analysis of iron (Review) 437
Bolton, H. C. Evolution of the thermometer (Review) 348
Bowers, H. L. See *Shober, W. B.*
Bredig, G. Anorganische Fermente (Review) 517
Brown, J. W. See *Mulliken, S. P.*
Buckingham, E. An outline of the theory of thermodynamics (Review) 171

CALDWELL, B. P. See *Jones, H. C.*
Canter, H. Orthophenylsulphobenzoic acid and related compounds 96
Classen, A. Ausgewählte Methoden der analytischen Chemie (Review) 437
Clover, A. M. See *Freer, P. C.*
Clowes and *Coleman.* Quantitative chemical analysis (Review) 251
Conn, W. T. See *Michael, A.*
de la Coux, H. L'Eau dans l'Industrie (Review) 81

ERDMANN, H. Lehrbuch der anorganischen Chemie (Review) 250

FAY, H. and *North, E.* On the nature of lead amalgams 216
Fraps, G. S. The composition of a wood oil 26
" The determination of pentosans 501
Freer, P. C. and *Clover, A. M.* On the constituents of Jamaica dogwood 390
French, P. R. See *Mulliken, S. P.*

GARNER, W. W. See *Remsen, I.*
Gildemeister and *Hoffmann.* Die aetherischen Oele (Review) 169
" " " Volatile oils 168
Gomberg, M. On trivalent carbon 317
Gore, H. C. See *McPherson, W.*
Groves and *Thorp.* Chemical Technology (Review) 80

HALE, W. J. See *Phelps, I. K.*
Henderson, W. E. Symmetrical chlorides of *p*-nitro-*o*-sulphobenzoic acid 1
Hill, H. B. On dehydromucic acid 439
" and *Wheeler, A. S.* On the reduction of dehydromucic acid 463
Holmes, W. B. On the action of the chlorides of *o*-sulphobenzoic and of *p*-nitro-*o*-sulphobenzoic acids on urea 202
Hopkins, A. J. The crystallization of copper sulphate 413
Hopkins, E. Oil chemist's handbook (Review) 82
Hudson, E. J. See *Mabery, C. F.*

JONES, H. C., and *Caldwell, B. P.* Contributions to the study of aqueous solutions of double salts 349

LEWES, V. B. Acetylene (Review) 85
Lindsay, C. F. The conductivity of some double salts as compared with the conductivity of mixtures of their constituents 62

MABERY, C. F. and *Hudson, E. J.* On the composition of California petroleum 253
" " *Sieplein, O. J.* On the chlorine derivatives of the hydrocarbons in California petroleum 284
" " *Takano, S.* On the composition of Japanese petroleum 297

Mallet, J. W. On the formation of platinum tetrachloride from aqueous hydrochloric acid by atmospheric oxidation in contact with platinum black........ 430
McPherson, W., and *Gore, H. C.* The constitution of the oxyazo compounds... 485
Michael, A. On methyl cyanide as a catalytic reagent........ 419
" and *Conn, W. T.* On the behavior of iodine and bromine towards chlorine heptoxide and perchloric acid........ 89
Miller, A. S. A manual of assaying (Review)........ 249
Moses and *Parsons.* Mineralogy, crystallography, and blowpipe analysis (Review)........ 250
Mulliken, S. P., Brown, J. W., and *French, P. R.* On the importance of formic aldehyde as a product of the partial combustion of organic compounds........ 111

NICHOLS, H. W. A new test for chlorine for use with the blowpipe........ 315
Norris, J. F. On the non-existence of trivalent nitrogen........ 117
" and *Sanders, W. W.* On triphenylchlormethane........ 54
North, E. See *Fay, H.*

O'BYRNE, L. See *Tingle, J. B.*
Ostwald, W. Grundlinien der anorganischen Chemie (Review)........ 83

PHELPS, I. K., and *Hale, W. J.* On dehydromucic acid and certain of its derivatives........ 445

RAOULT, F. M. (Obituary Notice)........ 510
Remsen, I., and *Garner, W. W.* On the action of aromatic sulphonchlorides on urea........ 173
" " *Turner, H. J.* On the action of aromatic sulphonchlorides on thiourea........ 190
Richards and *Woodman.* Air, water, and food (Review)........ 347
Richardson, G. M. The constitution of benzene........ 123
van Rijn, J. J. L. Die Glykoside (Review)........ 170
Russell, G. W. An easily constructed barometer........ 508
SADTLER, S. P. Industrial organic chemistry (Review)........ 169
Sanders, W. W. See *Norris, J. F.*
Shober, W. B., and *Bowers, H. L.* The action of sulphuric acid on phenetol........ 69
Sieplein, O. J. See *Mabery, C. F.*
Stillman, T. B. Engineering Chemistry (Review)........ 517

TAKANO, S. See *Mabery, C. F.*
Tillman, S. E. A text-book of important minerals and rocks (Review)........ 249
Tingle, A. The synthesis of amines by the use of alkyl salicylates........ 144
Tingle, J. B. and *O'Byrne, L.* Action of phenols on ethylic oxalate........ 496
Turner, H. J. See *Remsen, I.*
WHEELER, A. S. See *Hill, H. B.*

SUBJECTS.

ACETYLENE. *Lewes* (Review)........ 85
Aetherischen Oele, die. *Gildemeister* und *Hoffmann* (Review)........ 169
Air, water, and food. *Richards* and *Woodman* (Review)........ 347
Amines, the synthesis of, by means of alkyl salicylates. *A. Tingle*........ 144
    Action of ammonia gas with methylic, ethylic, and isoamylic salicylates; of aniline with methylic salicylate and benzoate, methylic hydroxybenzoates; of acetanilide with isoamyl salicylate.
Ammonium amalgam (Note)........ 431

Ammonium bromide and the atomic weight of nitrogen (Note)........ 167

Analytische Chemie, ausgewählte Methoden der. *Classen* (Review)........ 437

Anorganische Fermente. *Bredig* (Review)........ 517

Anorganischen Chemie, Grundlinien der. *Ostwald* (Review)........ 83

Anorganischen Chemie, Lehrbuch der. *Erdmann* (Review)........ 250

Argon and its companions (Note)........ 156

Assaying, a manual of. *Miller, A. S.* (Review)........ 249

Asymmetric optically active sulphur compounds (Note)........ 167

Atmosphere, combustible gases in the (Report)........ 344

Atomic structure, a recent review of (Report)........ 340

Atomic weights, international (Report)........ 335

BAROMETER, an easily constructed. *G. W. Russell*........ 508

Benzene, the constitution of. *G. M. Richardson*........ 123

Discussion of substitution, reduction and oxidation of benzene.

Bismuth, basic nitrates of. *F. B. Allan*........ 307

A study of compounds formed under different conditions.

CENTENARY Commemoration lecture at the Royal Institute of Great Britain (Note)........ 161

Chemical technology. *Groves* and *Thorp* (Review)........ 80

Chlorine, a new test for, for use with the blowpipe. *H. W. Nichols*........ 315

By use of paper wet with cobalt nitrate.

Combustible gases in the atmosphere (Report)........ 344

Commercial organic analysis. *A. H. Allen* (Review)........ 88

Copper sulphate, crystallization of. *A. J. Hopkins*........ 413

Conditions necessary to control crystallization.

DEHYDROMUCIC acid. *H. B. Hill*........ 439

Preparation of the acid and study of its reduction products.

Dehydromucic acid and certain of its derivatives. *I. K. Phelps* and *W. J. Hale.* 445

Preparation of the acid and K, Ba, and Ca salts, monomethyl and monoethyl compounds, acid amide, dianilide, diacetic anhydride, anhydride; action of halogens; prep. of $\alpha\alpha'$-dibenzoyl furfuran, $\alpha\alpha'$-dibenzoyl furfuran dihydrazone, $\alpha\alpha'$-dibenzoylfurfuran dioxime.

Dehydromucic acid, on the reduction of. *H. B. Hill* and *A. S. Wheeler*........ 463

Prep. of α,β- and γ-dihydrofurfuran-$\alpha\alpha'$-dicarboxylic acid and salts; action of nitric acid and potassium permanganate on the acid; action of bromine and action of barium hydroxide on the α-dibromide; action of chlorine on acid.

Dissociating power of different solvents (Report)........ 232

Double salts, contributions to the study of aqueous solutions of. *H. C. Jones* and *B. P. Caldwell*........ 349

Conductivityof K_2CdI_4, $SrCdI_4.8H_2O$, $2KCN.Hg(CN)_2$; $2NH_4NO_3Pr(NO_3)_3$; $2NH_4NO_3.Nd(NO_3)_3$; $(NH_4)_2SO_4.MgSO_4$; $(NH_4)_2SO_4.CuSO_4$; $(NH_4)_2SO_4.FeSO_4.6H_2O$; $(NH_4)_2SO_4.CdSO_4.6H_2O$; $(NH_4)_2SO_4.NiSO_4$; $K_2SO_4.NiSO_4$; cryoscopic measurements of $K_2Hg(CN)_4$; K_2CdI_4; $(NH_4)_2SO_4.CdSO_4$; $(NH_4)_2SO_4.CuSO_4$; $2NH_4NO_3.Pr(NO_3)_3$.

Double salts, the conductivity of some, as compared with the conductivities of their constituents. *C. F. Lindsay*........ 62

Experiments with chlorides and sulphates.

L'EAU dans l'Industrie. *H. de la Coux* (Review)........ 81

Engineering Chemistry. *Stillman*........ 517

Ethylic oxalate, action of phenols on. *J. B. Tingle* and *L. O'Byrne*........ 496

Experiments with pyrocatechol, carvacrol, picric acid, β-naphthol, ethylic salicylate, quinone, guaiacol, resorcin, phloroglucinol, hydroquinol, anisoïl, and carvol.

FLUOSILICIC acid as a preservative of manure (Note)........................ 166
Formic aldehyde, on the importance of, as a product of the partial combustion of organic compounds. *S. P. Mulliken, J. W. Brown*, and *P. R. French*.. 111
Formation from a number of organic compounds.
GLYKOSIDE, die. *J. J. L. van Rijn* (Review).................................. 170

HYDROGEN, the higher superoxides of (Report)............................. 336
Hydrogen, the liquefaction of (Note).. 160

INDUSTRIAL organic chemistry. *S. P. Sadtler* (Review)..................... 169
Iodine and bromine, on the behavior of, towards chlorine heptoxide and perchloric acid. *A. Mickael* and *W. T. Conn*........ 89
Chlorine is not replaced by bromine nor is perbromic acid formed.
Iron, the chemical analysis of. *A. A. Blair* (Review).......................... 437

JAMAICA dogwood, on the constituents of. *P. C. Freer* and *A. M. Clover*...... 390
Isolation of piscidic acid, its ethyl ester and anilide and compounds of the composition $C_{20}H_{22}O_7$, $C_{22}H_{18}O_6$, and $C_{23}H_{20}O_7$.

LAVOISIER statue in Paris, the (Note)......................... 435
Lead amalgams, on the nature of. *H. Fay* and *E. North*........................ 216
Study of fusibility and microstructure.

METHYL cyanide as a catalytic agent, and a criticism of J. U. Nef's views on the Frankland, Wurtz, and Conrad reactions. *A. Michael*.............. 419
Mineralogy, crystallography, and blowpipe analysis. *Moses* and *Parsons* (Review... 250
Minerals and rocks, a text-book of important. *S. E. Tillman* (Review)........ 249

NOTES:
- Ammonium amalgam.. 431
- Ammonium bromide and the atomic weight of nitrogen 167
- Argon and its companions............ 156
- Asymmetric optically active sulphur compounds 167
- Centenary commemoration lecture at the Royal Institute of Great Britain.. 161
- Fluosilicic acid as a preservative of manure............................ 166
- Hydrogen, the liquefaction of.. 160
- Lavoisier statue in Paris, the.. 435
- Oxyazo-compounds, on the nature of the.............. 80
- Ozone, the density and molecular weight of............................ 432
- Radio-active substances, the new......................... 77

OBITUARY notice. *F. M. Raoult*............ 510
Oil chemist's handbook. *E. Hopkins* (Review) 82
Orthophenylsulphonebenzoic acid and related compounds. *H. Canter*........ 96
Prep. and props. of orthotolylphenylsulphone, orthophenylsulphonebenzoic acid, its salts, chloride, amide, anilide ; orthobenzoyldiphenylsulphone.
Orthosulphobenzoic and *p*-nitro-*o*-sulphobenzoic acids on urea, the action of the chlorides of. *W. B. Holmes*.............. 202
Prep. of chlorides of the ortho acid and action of urea with the formation of the ammonium salt of benzoylureaorthosulphonic acid ; action of hydrochloric acid, caustic potash, and barium hydroxide on this salt ; prep. of free acid and salts ; action with chlorides of the paranitro acid with formation of corresponding paranitro salt ; prep. of free acid and salts.
Oxyazo compounds, on the nature of the (Note)............................... 80
Oxyazo compounds, the constitution of the. *W. McPherson* and *H. C. Gore*.... 485
Prep. of α-benzoyl-α-naphthylhydrazine and its action on paraquinones of the benzene series.

Ozone, the density and molecular weight of (Note) 432

PARANITROORTHOSULPHOBENZOIC acid, symmetrical chlorides of. *W. E. Henderson*........................ 1
  Action of aluminium chloride and benzene with formation of *p*-nitro-*o*-benzoylbenzenesulphone chloride; action of alcohols and formation of the acid ethereal salt; action of phenols and formation of the diphenyl ester and sulphonphthaleins; action of aniline and formation of the anilide and anil; with phosphorus oxychloride with formation of dianil; action of hydrochloric acid, alcoholic potash, and glacial acid on the dianil.
Pentosans, the determination of. *G. S. Fraps*........................ 501
  The formation of furaloid from action of hydrochloric acid on vegetable substances.
Petroleum, on the composition of California and Japanese and the chlorine compounds of. *C. F. Mabery*, *E. J. Hudson*, and *S. Takano*........ 253, 284, 297
  Isolation of hydrocarbons and determination of properties.
Phenetol, the action of sulphuric acid on. *W. B. Shober* and *H. L. Bowers*..... 69
  Formation of para and metaphenetolsulphonic acid and phenetoldisulphonic acid.
Platinum tetrachloride, on the formation of, from aqueous hydrochloric acid by atmospheric oxidation in contact with platinum black. *J. W. Mallet*........................ 430

QUANTITATIVE chemical analysis. *Clowes* and *Coleman* (Review)........... 251

RADIO-ACTIVE substances, the new (Note)........................ 77
Reports:
  Atomic structure, a recent review of........................ 340
  Atomic weights, international........................ 335
  Combustible gases in the atmosphere........................ 344
  Dissociating power of different solvents........................ 232
  Hydrogen, the higher superoxides of........................ 336
  Rocks, the action of water upon........................ 511
Reviews:
  Acetylene. *V. B. Lewes*........................ 85
  Aetherischen Oele, die. *Gildemeister* und *Hoffmann*........................ 169
  Air water, and food from a sanitary standpoint. *Richards and Woodman*........................ 347
  Analytische Chemie, Ausgewählte Methoden der. *A. Classen*.......... 437
  Anorganische Fermente. *G. Bredig*........................ 517
  Anorganischen Chemie, Grundlinien der. *W. Ostwald*........................ 83
  Anorganischen Chemie, Lehrbuch der. *H. Erdmann*........................ 250
  Assaying, a manual of. *A. S. Miller*........................ 249
  Chemical technology. *Groves* and *Thorp*........................ 80
  Commercial organic analysis, Vol. III., Part I. Tannins, dyes, and inks. *A. H. Allen*........................ 88
  l'Eau dans l'Industrie. *H. de la Coux*........................ 81
  Engineering chemistry. *T. B. Stillman*........................ 517
  Glykoside, die. *J. J. L. van Rijn*........................ 170
  Industrial organic chemistry, a handbook of. *S. P. Sadtler*............ 169
  Iron, the chemical analysis of. *A. A. Blair*........................ 437
  Mineralogy, crystallography, and blowpipe analysis, elements of. *Moses* and *Parsons*........................ 250
  Minerals and rocks, a text-book of important. *S. E. Tillman*.......... 249
  Oil chemist's handbook. *E. Hopkins*........................ 82
  Quantitative chemical analysis. *Clowes* and *Coleman*........................ 251
  Thermodynamics, an outline of the theory of. *E. Buckingham*......... 171

Thermometer, evolution of the. *H. C. Bolton* 348
Volatile oils, the. *Gildemeister* and *Hoffmann* 168
Rocks, the action of water upon (Report) 511

SULPHONCHLORIDES on thiourea, action of aromatic. *I. Remsen* and *H. J. Turner* 190
Action of benzenesulphonchloride with formation of dithiourea dichloride and benzenedisulphoxide and properties of these compounds; action of *p*-toluenesulphonchloride withformation of paratoluenedisulphoxide; action of ammonium sulphocyanate and benzenesulphonchloride; action of potassium benzenesulphinate on dithiocarbamide dichloride.
Sulphonchlorides on urea, action of aromatic. *I. Remsen* and *W. W. Garner* 173
Action of benzenesulphonchloride with formation of guanylureabenzenesulphonate; action of hydrochloric and nitric acids, barium hydrate and potassium carbonate on this substance; action of *p*-toluenesulphonchloride with formation of guanylurea *p*-toluenesulphonate, action of hydrochloric and nitric acids; action of ortho compound with similar results; action of α- and β-naphthalenesulphonchloride with formation of corresponding sulphonate.

THERMODYNAMICS, an outline of the theory of. *E. Buckingham* (Review). 171
Thermometer, evolution of the. *H. C. Bolton* (Review) 348
Triphenylchlormethane. *J. F. Norris* and *W. W. Sanders* 54
Prep. of the compound and isolation of an intermediate aluminium compound.
Trivalent carbon. *M. Gomberg* 317
Defence of previous work.
Trivalent carbon, on the non-existence of. *J. F. Norris* 117
Action of metals on triphenylchlormethane.

VOLATILE oils. *Gildemeister* and *Hoffmann* (Review) 168

WOOD-OIL, the composition of a. *G. S. Fraps* 26
Separation of ketones and aldehydes by acid sodium sulphite; isolation of ethereal salts, furanes, and aromatic hydrocarbons.

FORMULA.

C_1-GROUP.

$CH_4O_2N_4$. Nitroguanidine. *I. Remsen* and *W. W. Garner* 178
Prep. from guanylureabenzenesulphonate.

C_2-GROUP.

$C_2H_8N_4Cl_2S_2$. Dithiourea dichloride. *I. Remsen* and *H. J. Turner* 193
Prep. from sulphourea and benzenesulphonchloride.

C_4-GROUP.

$C_4H_2OBr_6$. Dibromfurfurantetrabromide. *I. K. Phelps* and *W. J. Hale* 445
Prep. from dehydromucic acid and dibromfurfuran tetrabromide.

C_5-GROUP.

C_5H_6O. Methylfurane. *G. S. Fraps* 41
C_5H_8O. Adipic ketone. *G. S. Fraps* 33

C_6-GROUP.

$C_6H_4O_5$. Dehydromucic acid. *I. K. Phelps* and *W. J. Hale* 445
Prep. of acid and salts.

$C_6H_6O_5$. α-, β- and γ-Dihydrofurfuran-αα′-dicarboxylic acid. *H. B. Hill* and *A. S. Wheeler* 463
Prep. from dehydromucic acid.

6 III.

$C_6H_5O_4N$. Dehydromucic acid amide. *I. K. Phelps* and *W. J. Hale* 445
Prep. from acid ethyl ester and ammonia.

$C_6H_7O_6Cl$. α-, β- and γ-Chlorhydroxytetrafurfuran-αα-dicarboxylic acid. *H. B. Hill* and *A. S. Wheeler* 463
Prep. from the α-acid.

$C_6H_6O_5Br_2$. α-, β- and γ-Dihydrofurfuran-αα′-dicarboxylicdibromide. *H. B. Hill* and *A. S. Wheeler* 463
Prep. from the α-acid and bromine.

$C_6H_{12}O_2N_2$. Dimethyl furane. *G. S. Fraps* 44

C_7-GROUP.

$C_7H_6O_5$. Monomethyldehydromucate. *I. K. Phelps* and *W. J. Hale* 445
Prep. from dimethyldehydromucate.

7 III.

$C_7H_5O_2Br$. Brombenzoic acid. *I. K. Phelps* and *W. J. Hale* 445

$C_7H_{14}O_2N_2$. Trimethylfurane. *G. S. Fraps* 44

7 IV.

$C_7H_8O_7N_2S$. Acid ammonium salt of *p*-nitro-*o*-sulphobenzoic acid. *W. B. Holmes* 212

$C_7H_{11}O_3N_3S$. Guanidine benzenesulphonate. *I. Remsen* and *W. W. Garner* 177
Prep. from guanylurea benzenesulphonate and hydrochloric acid.

7 V.

$C_7H_3O_5NCl_2S$. Chlorides of *p*-nitro-*o*-sulphobenzoic acid. *W. E. Henderson* 48

C_8-GROUP.

$C_8H_8O_5$. Monomethyldehydromucate. *I. K. Phelps* and *W. J. Hale* 445
Prep. from diethylester.

8 IV.

$C_8H_7O_7NS$. Ethereal salt of *p*-nitro-*o*-sulphobenzoic acid. *W. E. Henderson*

$C_8H_7O_7N_3S$. Paranitrobenzoylurea-*o*-sulphonic acid. *W. B. Holmes* 213
Prep. from Ba salt and formation of K, Na, Pb, Cu, and Ag salts.

$C_8H_8O_5N_2S$. Benzoylurea-*o*-sulphonic acid. *W. B. Holmes* 207
Prep. from the ammonium salt and formation of K, Na, Pb, Cu, and Ag salts.

$C_8H_{10}O_7N_4S$. Ammonium salt of *p*-nitrobenzoylurea-*o*-sulphonic acid. *W. B. Holmes* 221
Prep. from urea and the chloride of the acid.

$C_8H_{11}O_5N_3S$. Ammonium salt of benzoylurea-*o*-sulphonic acid. *W. B. Holmes* 206
Prep. from urea and chloride of *o*-sulphobenzoic acid.

$C_8H_{12}O_4N_2S$. Sulphonate of urea. *I. Remsen* and *W. W. Garner*................ 186
Prep. from urea and *p*-toluenesulphonchloride.

$C_8H_{12}O_4N_4S$. Guanylurea benzenesulphonate. *I. Remsen* and *W. W. Garner*. 176
Prep. from urea and benzenesulphonchloride.

$C_8H_{18}O_8N_3S$. Guanidine *p*-toluenesulphonate. *I. Remsen* and *W. W. Garner*.. 183
Prep. from guanylurea *p*-toluenesulphonate.

C_9-GROUP.

$C_9H_{14}O_4N_4S$. Guanylurea *o*- and *p*-toluenesulphonate. *I. Remsen* and *W. W. Garner*.. 182, 186
Prep. from urea and the sulphonchloride.

C_{10}-GROUP.

$C_{10}H_8O_7$. Dehydromucic-diacetic anhydride. *I. K. Phelps* and *W. J. Hale* 445
Prep. from acid and acetic anhydride.

C_{11}-GROUP.

$C_{11}H_{12}O_7$. Piscidic acid. *P. C. Freer* and *A. M. Clover*........................ 329
Isolation from Jamaica dogwood.

C_{12}-GROUP.

$C_{12}H_4O_8$. Dehydromucic anhydride. *I. K. Phelps* and *W. J. Hale* 445
Prep. from the acid.

12 III.

$C_{12}H_{10}O_2S_2$. Benzene disulphoxide. *I. Remsen* and *H. J. Turner*... 196
Prep. from sulphourea and benzenesulphonchloride.

12 IV.

$C_{12}H_{14}O_4N_4S$. Guanylurea α- and β-naphthalenesulphonate. *I. Remsen* and *W. W. Garner*... 187
Prep. from urea and the chloride.

C_{13}-GROUP.

$C_{13}H_{10}O_4S$. Orthophenylsulphonebenzoic acid. *H. Canter* 99
Prep. from orthotolylphenylsulphone.

$C_{13}H_{12}O_2S$. Orthotolylphenylsulphone. *H. Canter* 97

13 IV.

$C_{13}H_9O_3ClS$. Orthophenylsulphonebenzoyl chloride. *H. Canter* 104
Prep. from a salt of the acid.

$C_{13}H_{10}O_6N_2S$. Anilide of *p*-nitro-*o*-sulphobenzoic acid. *W. E. Henderson*....... 21

$C_{13}H_{11}O_3NS$. Orthophenylsulphonebenzamide. *H. Canter* 105
Prep. from the chloride.

C_{14}-GROUP.

$C_{14}H_{14}O_2S_2$. Paratoluenedisulphoxide. *I. Remsen* and *H. J. Turner* 198
Prep. from *p*-toluenedisulphonechloride and sulphourea.

C_{16}-GROUP.

$C_{16}H_{12}ON_2$. α-Naphthaleneazophenol. *W. McPherson* and *H. C. Gore*.......... 490
Prep. from diazo-α-naphthalene hydrochloride and phenol.

C_{17}-GROUP.

$C_{17}H_{14}ON_2$. α-Naphthaleneazoorthocresol. *W. McPherson* and *H. C. Gore*..... 493
Prep. from diazo α-naphthalenehydrochloride and orthocresol.

$C_{17}H_{14}ON_2$. α-Benzoyl-α-naphthylhydrazine. *W. McPherson* and *H. C. Gore*.. 488
Prep. from α-acetylnaphthylhydrazine.

C_{18}-GROUP.

$C_{18}H_{12}O_3$. αα'-Dibenzoylfurfuran. *I. K. Phelps* and *W. J. Hale* 445
Prep. from dehydromucylchloride and benzol.

18 III.

$C_{18}H_{14}O_3N_2$. αα'-Dibenzoylfurfurandioxime. *I. K. Phelps* and *W. J. Hale* 445
Prep. from hydroxylamine and the ketone.

$C_{18}H_{14}O_3N_2$. Dehydromucic dianilide. *I. K. Phelps* and *W. J. Hale* 445
Prep. from dehydromucylchloride and aniline.

C_{19}-GROUP.

$C_{19}H_{15}Cl$. Triphenylchlormethane. *J. F. Norris* and *W. W. Sanders*.......... 60

19 IV.

$C_{19}H_{13}O_4N_3S$. Dianil of *p*-nitro-*o*-sulphobenzoic acid. *W. E. Henderson* 23

$C_{19}H_{13}O_7NS$. Diphenylester of *p*-nitro-*o*-sulphobenzoic acid. *W. E. Henderson* 12

$C_{19}H_{13}O_9NS$. Sulphonphthalein from the chloride of *p*-nitro-*o*-sulphonbenzoic acid. *W. E. Henderson*...... 17

$C_{19}H_{15}O_3NS$. Orthophenylsulphonebenzanilide. *H. Canter* 106
Prep. from the chloride and aniline.

$C_{19}H_{15}O_5N_3S$. Anil of *p*-nitro-*o*-sulphobenzoic acid. *W. E. Henderson* 21

C_{20}-GROUP.

$C_{20}H_{22}O_7$. Substance extracted from Jamaica dogwood. *P. C. Freer* and *A. M. Clover* 406

20 III.

$C_{20}H_{20}ON_2$. α-Naphthaleneazothymol. *W. McPherson* and *H. C. Gore*......... 495
Prep. from α-naphthylamine.

C_{21}-GROUP.

$C_{21}H_{17}O_7NS$. Product of action of paracresol on the chloride of *p*-nitro-*o*-sulphobenzoic acid. *W. E. Henderson* 15

C_{22}-GROUP.

$C_{22}H_{18}O_6$. Substance extracted from Jamaica dogwood. *P. C. Freer* and *A. M. Clover* 403

C_{23}-GROUP.

$C_{23}H_{20}O_7$. Substance extracted from Jamaica dogwood. *P. C. Freer* and *A. M. Clover* 400

23 III.

$C_{23}H_{16}O_2N_2$. Benzoate of α-naphthaleneazophenol. *W. McPherson* and *H. C. Gore* 492
Prep. from naphthaleneazophenol.

$C_{23}H_{16}O_2N_2$. Quinone benzoyl-α-naphthylhydrazone. *W. McPherson* and *H. C. Gore* 489
Prep. from the benzoquinone and hydrazone.

C_{24}-GROUP.

$C_{24}H_{18}O_2N_2$. Benzoate of α-naphthaleneazoorthocresol. *W. McPherson* and *H. C. Gore* 494
Prep. from the azocresol and benzoylchloride.

$C_{24}H_{18}O_2N_2$. Toluquinone benzoyl-α-naphthylhydrazone. *W. McPherson* and *H. C. Gore* 492
Prep. from toluquinone and α-benzoyl-α-naphthylhydrazine hydrochloride.

C_{27}-GROUP.

$C_{27}H_{24}O_2N_2$. Thymoquinone benzoyl-α-naphthylhydrazone. *W. McPherson* and *H. C. Gore* 494
Prep. from thymoquinone and α-benzoyl-α-naphthylhydrazine hydrochloride.

$C_{27}H_{24}O_2N_2$. Benzoate of α-naphthaleneazothymol. *W. McPherson* and *H. C. Gore* 496
Prep. from α-naphthaleneazothymol.

C_{30}-GROUP.

$C_{30}H_{24}ON_4$. αα'-Dibenzoylfurfurandihydrazone. *I. K. Phelps* and *W. J. Hale* . 445

UNIVERSITY OF ILLINOIS-URBANA
3 0112 057094069